

INTERNAL LOADING IN SHALLOW LAKES

By

CURTIS DEVIN POLLMAN

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

1983

ACKNOWLEDGMENTS

Support from numerous sources assisted me during the course of my studies. Charles Hendry, Tom Belanger, Carl Miles, and Charles Fellows all sacrificed time and effort in accommodating me during the field portion of my studies. Further appreciation is extended to Charles Hendry for introducing me to some of the subtle nuances of the analytical equipment critical to the success of this research.

I am deeply grateful for the support of my chairman, Dr. P.L. Brezonik whose continued faith, gentle proddings, and guidance helped provide the inspiration to complete my research. I also wish to acknowledge the other members of my graduate committee, Dr. Wayne C. Huber, Dr. Donald Graetz, Dr. Edward S. Deevey, and Dr. Thomas L. Crisman, whose critical review and comments helped produce the final manuscript. Dr. A.J. Mehta and Dr. Gregory M. Powell both provided invaluable help in approaching the development of a sediment resuspension model.

Eileen Town, who typed the initial and final manuscripts, deserves special recognition for her professional competence and perserverance. Appreciation is also extended to Carla S. Jones and Marlene A. Hobel for putting up with the neurotic antics of an expectant author and providing the finishing touches to the manuscript.

I particularly wish to thank my parents, Mr. and Mrs. Ralph C. Pollman, and my grandmother, Mrs. Harold G. Lengerich, for spiritually and financially sustaining me during the ebb moments of my graduate career. My wife Kathleen sacrificed much for the sake of my work and is especially deserving of recognition. Without her support and encouragement, this work doubtlessly would have remained uncompleted. Finally, I wish to dedicate this work to the memory of my twin brother, Chris, whose recent departure from life instilled in the author a sense of necessity. His spiritual guidance was prodigious and is profoundly missed.

TABLE OF CONTENTS

	PAGE
ACKNOWLEDGMENTS.	ii
ABSTRACT	vi
CHAPTER	
I INTRODUCTION	1
Forms of Sedimentary Phosphorus.	2
Mechanisms of Nutrient Release	6
Bioturbation	6
Gas Ebullition	8
Sediment Resuspension.	10
Molecular Diffusion.	13
Summary.	15
II SITE DESCRIPTION AND METHODOLOGY	17
Physical Description and Limnology of Lake Okeechobee.	17
Physical Description and Limnology of Lake Apopka.	25
Materials and Methods.	29
Physical and Chemical Characterization	29
Sorption Experiments	34
III PHYSICAL-CHEMICAL SEDIMENT CHARACTERISTICS	35
Physical Characteristics	35
Chemical Characteristics	47
IV RELEASE STUDIES.	57
Turbulence Study	71
Fresh Sediment	72
Partially Dessicated Sediment.	78
In Situ Studies.	80

	PAGE
V	
NUTRIENT RELEASE MODEL	92
Development of a Langmuir Sorption Model	97
Application of Langmuir Model to Lake Apopka and Lake Okeechobee Sediments.	108
Equilibrium Phosphorus Concentration (EPC)	118
Desorption	123
Effect of pH on P Sorption by Lake Okeechobee and Lake Apopka Sediments.	127
Development of a Sediment Resuspension Phosphorus Release Model for Lake Okeechobee and Lake Apopka. .	131
Nutrient Release Submodel.	131
Sediment Resuspension Model.	133
Calculation of Wind-Induced Stress at the Sediment-Water Interface	134
Determination of Critical Shear Stress	137
Calculation of Sediment Resuspension Rates	142
Sediment Dispersion Model.	144
Application of the Integrated Model to Lake Apopka and Lake Okeechobee.	150
VI	
DISCUSSION AND SUMMARY	161
Discussion of Internal Loading	161
Summary.	174
REFERENCES	178
BIOGRAPHICAL SKETCH.	191

Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

INTERNAL LOADING IN SHALLOW LAKES

By

Curtis Devin Pollman

April 1983

Chairman: Patrick L. Brezonik

Major Department: Environmental Engineering Sciences

Internal loading of phosphorus may be significant in shallow lakes where physical and biological processes can accelerate rates of solute exchange across the sediment-water interface. Sediments were collected from Lake Apopka and Lake Okeechobee located in central and south Florida, respectively, and characterized with respect to physical and chemical attributes of the sediment that control the dynamics of phosphorus exchange between sediments and overlying water. A series of experiments were conducted on bulk sediment to determine rates of phosphorus exchange across the sediment-water interface as a function of turbulence and physical state of the sediment.

The shallow nature and broad fetch characteristic of Lake Apopka (mean depth 1.7 m) and Lake Okeechobee (mean depth 2.8 m) suggest that

sediment resuspension and the concomitant release of sorbed phosphorus may be important in the cycling of phosphorus. As a result, a model was developed incorporating physical, chemical, and hydrodynamic components to predict internal loading of phosphorus in shallow lakes. Phosphorus releases are predicted on a single event basis in response to wind-driven turbulent mixing in the water column. The model synthesizes a wave-hindcasting submodel to determine sediment resuspension rates and a phosphorus release submodel derived from Langmuir sorption theory. Langmuir constants used as model inputs were derived from adsorption-desorption isotherms conducted at controlled pH.

Under ambient conditions in the water column, both Lake Apopka and Lake Okeechobee sediments are predicted to release phosphorus upon resuspension. Results indicate that a moderate wind event (approximately 8.9 m/s) can more than double mid-lake concentrations of orthophosphorus in Lake Apopka from 20 to 61 ug P/L at pH 8.3. Phosphorus release from Lake Okeechobee sediments is substantially lower (approximately 3 to 8 ug P/L). Release is primarily from desorptive processes; however, in Lake Apopka entrained pore fluid contributes approximately 30 percent of the net release. The cumulative effect of cyclonic and convective disturbances during the course of a year results in internal loading in Lake Apopka easily exceeding external loading rates. Sediment resuspension is less significant in Lake Okeechobee, and the nutrient regime appears to be controlled primarily by external loading.

CHAPTER I INTRODUCTION

Within the past two decades, the widespread recognition of lake degradation as an issue of major environmental concern has spawned accelerated efforts to better protect and manage lake resources (Born 1979; U.S. EPA 1979). Phosphorus has been implicated as the most important nutrient limiting phytoplankton growth and production in many freshwater lakes (Vollenweider 1968; Vallentyne 1970; Likens 1972; Schindler 1977). Consequently, many lake restoration schemes have focused on curbing external or cultural input of phosphorus to lacustrine systems.

In the decade following the introduction of Vollenweider's (1968) now classic paper, great emphasis was placed by limnologists on modeling one factor that influences productivity--external nutrient loading. In spite of the emphasis given this narrow focal point, interest also has been sustained in observing the contribution of phosphorus from lake sediments to the overlying water--"internal loading" (cf. Golterman 1977). Much of this work was inspired by early studies such as those conducted by Mortimer (1941, 1942) on Esthwaite Water in the English Lake District. More recent work by Fee (1979) has rekindled speculation and debate on the importance of lake morphometry to lake trophic state and, in particular, the area of sediment in direct contact with the trophogenic zone.

Lacustrine sediments may consist of up to 0.75 percent (by weight) phosphorus (Jones and Bowser 1978). This nutrient pool represents a potential source of supply to the overlying water column approximating 8 g P/m^2 for each centimeter of the sediment column actively engaged in exchange across the mud-water interface. In view of the work of Vollenweider (1968, 1975, 1976) and others in defining critical areal nutrient loading rates, it becomes quite evident that the availability of sedimentary phosphorus for exchange and the factors that mediate the transfer of the available pool, both abiotic and biotic, may have a profound influence on the nutrient regime of a lake. The following section is thus devoted to a discussion of the chemical nature of sedimentary phosphorus and its availability for exchange and biological uptake; factors that control the rate of exchange across the sediment-water interface are discussed in subsequent sections.

Forms of Sedimentary Phosphorus

A variety of analytical techniques has been used to fractionate sedimentary P with the ultimate objective of correlating a defined fraction with biological response (i.e., nutrient uptake). Early fractionation schemes borrowed heavily from the pioneering work in soils by Chang and Jackson (1957). Perhaps the most definitive work on lacustrine sediments to supersede the efforts of Chang and Jackson (1957) in soils was that of Williams et al. (1971). Williams et al. (1971) operationally defined four distinct species of sedimentary P: (1) inorganic P present as orthophosphate ion sorbed on surfaces of P retaining minerals (nonoccluded P); (2) inorganic P present as a

coprecipitate or minor component of an amorphous phase (occluded P); (3) orthophosphate P present in discrete phosphatic minerals such as apatite $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where $\text{X} = \text{OH}^-$, F^- , or $1/2 \text{CO}_3^{2-}$; and (4) P present as an organic ester or directly bonded to carbon atoms (organic P). The chemical nature of sedimentary P has been the subject of rather intensive reviews by both Jones and Bowser (1978) and Armstrong (1979).

In more recent work by Williams et al. (1976), the categorization of sedimentary P has been reduced to three major types: (1) organic phosphorus, which encompasses all P associated with organic material via C-O-P or C-P bonds; (2) apatite P comprised of orthophosphorus present within the crystalline lattice of apatite grains; and (3) nonapatite inorganic phosphorus (NAI-P) which consists of the remaining orthophosphorus fraction including that dissolved in the interstitial solution. This latter category constitutes the most labile fraction and is generally associated with exchangeability. In the development of these categories, Williams et al. (1976) assumed that nonorthophosphatic forms of inorganic phosphorus, e.g., polyphosphate ions (including pyrophosphate) are present in sediments only in negligible quantities.

Isotopic exchange studies conducted by Li et al. (1972) using P-32 as a tracer provide direct evidence that a substantial fraction of the total inorganic pool in sediments is exchangeable. Exchangeable P comprised 19 to 43 percent of the total inorganic content of sediments derived from four Wisconsin lakes. Total exchangeable P was found to be relatively insensitive to changes in redox status; this was interpreted by Li et al. (1972) as consistent with the retention of inorganic P in sediments by an iron-rich gel complex (Williams et al. 1971;

Shukla et al. 1971). Li et al. (1972) hypothesize that although the equilibrium position between sorbed and free inorganic P for the iron gel complex is altered by a shift in redox potential, the total exchangeable pool is not appreciably increased. Conversely, if inorganic P existed primarily as a discrete crystalline iron phosphate such as strengite, total exchangeable P should increase significantly upon dissolution of the solid phase during anaerobiosis.

The high rate of exchangeability observed by Li et al. (1972) provides further qualitative evidence of the retention of inorganic P as a nonoccluded form through sorption to an amorphous iron hydrous oxide gel. Incorporation of P into a crystalline lattice is anticipated to yield a reduction of exchangeability primarily because of a reduction in surface area. Additional experiments conducted by Li et al. (1972) with sediments equilibrated with solutions spiked with orthophosphorus demonstrated equivalent degrees of exchange for sorbed and native inorganic P. The authors suggested that native inorganic P is retained in sediments by the same mechanism as sorbed P.

Alternative fractionation schemes to define the labile fraction of sedimentary P available for algal uptake have involved chelating agents, anion and cation exchange resins (Wildung and Schmidt 1973; Huettl et al. 1979), and desorption potential (Schaffner and Oglesby 1978). Golterman (1973) used 0.01 N NTA (nitrilotriacetic acid) to extract P associated with calcium (Ca) and iron (Fe) constituents in sediments. Golterman (1977) found essentially no difference between NTA extracted phosphorus and calculated P uptake by the alga Scenedesmus utilizing the

same sediment as its solitary source of P. Grobler and Davies (1979) found NTA-extractable P to generally be a more applicable measure of algal available P than total inorganic P. Although both fractions were correlated with algal uptake, the most consistent relationship was observed between P availability and NTA extractable P. A non-linear relationship between algal available P and sediment inorganic P was demonstrated by Grobler and Davies (1978); the fraction of inorganic P comprised by algal available P varied with sediment type and was quite variable, ranging from 4 to 98 percent.

As a means for differentiating between Fe-bound and Ca-bound P, Golterman (1977) proposed an initial extraction with 0.01 M Ca-NTA. According to Golterman, complexation of the added Ca by NTA prevents the solubilization of sedimentary calcium and extraction of Ca-P; consequently only iron-bound P is extracted. Subsequent work by Williams et al. (1980), however, does not support Golterman's contention that Ca-NTA selectively extracts Fe- and aluminum (Al)-associated P, leaving Ca-P intact. Extraction with a neutral, noncomplexing agent (1 M NaCl) yielded extraction efficiencies comparable with Ca-NTA. Extraction with Ca-NTA rarely exceeded 10 percent of the NAI-P fraction. Uptake of sedimentary P by S. quadricauda was closely correlated with the NAI-P fraction by Williams et al. (1980) and constituted approximately 75 percent of NAI-P; apatite-P was virtually unavailable for algal growth. These results qualitatively confirm the earlier observations of Grobler and Davies (1978), who noted that algal available P generally exceeded NTA-extractable P by a factor of approximately 5 to 6.

Mechanisms of Nutrient Release

As detritus accumulates in surficial deposits, metabolism of accreting organic material results in the buildup of interstitial phosphorus concentration to levels that exceed those in the overlying water by as much as several orders of magnitude. Release to the overlying water is accomplished by burrowing and irrigation activities of benthic organism (i.e., bioturbation), by gas ebullition from anaerobic decomposition processes, by scouring of the interface by wind-induced waves, and simply by molecular diffusion across the concentration gradient that usually exists between sediment pore water and the overlying water.

Bioturbation

Based on analysis of Pb-210 and Cs-137 profiles in recent sediments of the Great Lakes, Robbins and Edgington (1975) suggested that post-depositional movement of material occurred within the surficial 10 cm of sediment. Robbins and Edgington (1975) postulated that the observed redistribution of sediment particles was the result of either physical mixing or bioturbation. Activities of the benthic community, such as burrowing, irrigation, and feeding, result in fluid and particle transport near (and across) the sediment-water interface. Bioturbation increases the influx of water into sediments; this is balanced by an equal volume of interstitial solution flushed from sediments (Petr 1977). Hargrave and Connolly (1978) observed a great deal of spatial variability in nutrient and gas fluxes across the sediment-water interface of a subtidal flat and attributed the variability to heterogeneity

in the distribution of benthic macrofauna. Berger and Heath (1968) suggested that homogenization of the upper sediments is complete when sediment displacement by benthic infauna is comparable to or exceeds the sediment accumulation rate. As an extension of this assumption, Krezoski et al. (1978) used average defecation rates for Tubifex tubifex to estimate sediment displacement, and they calculated that oligochaete densities in profundal sediments of Lake Huron were sufficient to displace the upper 3 to 6 cm. Neame (1977) observed a total phosphorus flux of approximately $650 \text{ ug/m}^2\text{-d}$ across the surficial 3 cm of sediment in Castle Lake, California, and attributed this flux to chironomid activity in the oxidized zone of the sediments. Under anoxic conditions, the phosphorus flux across the interface decreased by two orders of magnitude.

Aller (1978) reported that benthic infauna activity affects the dynamics of the sediment-water exchange process by altering the geometry and kinetics of molecular diffusion in sediments. In the absence of benthic activity, Aller (1978) successfully used Berner's (1976) one-dimensional diffusion model to describe the vertical distribution of interstitial phosphorus in marine sediments. In the presence of the highly mobile protobranch, Yoldia limatula, pore-water transport was characterized by a non-steady-state two-layer model in which an effective (or biogenic) diffusion coefficient acts in the zone of feeding and molecular diffusion controls transport in underlying sediment. The effective biogenic diffusion coefficient for pore-water transport by Yoldia is approximately $1 \times 10^{-5} \text{ cm}^2/\text{s}$; this compares to a tortuosity-corrected molecular diffusion coefficient of

$2.4 \times 10^{-6} \text{ cm}^2/\text{s}$ for HPO_4^{-2} in undisturbed sediments. Lerman (1979) indicated that effective diffusion coefficients in the mixed layer are on the order of 5 to 100 times greater than the molecular diffusion coefficient.

Several other types of models have been developed to describe the effects of bioturbation on sediment-water solute exchange. Grundmanis and Murray (1977) and McCaffrey et al. (1980) suggested that transport can be simulated by assuming that interstitial water is biogenically advected between discrete well-mixed reservoirs within the sediment and overlying water. Aller (1978, 1980) proposed an idealized model which assumes that specific changes in the average geometry of molecular diffusion result from the presence of irrigated tube and burrow structures. Average interstitial concentrations, solute flux, and apparent one-dimensional diffusion coefficients are influenced by both the size and spacing of burrows.

Gas Ebullition

The evolution of gas bubbles within anaerobic sediments also may enhance the flux of dissolved constituents across the sediment-water interface. Two mechanisms have been proposed by Klump and Martens (1981) to explain the influence of gas ebullition on exchange. Bubble tube structures alter the geometry of the sediment-water interface and increase the surface area available for chemical exchange. If flow patterns at the interface permit unrestricted import and export of overlying water within tube structures, the total flux across the interface is increased. Conversely, restriction of flow may allow

solute concentrations within the tube to reach high concentrations, establishing a sharp vertical concentration gradient across the interface. Mixing of the pore water in the tube by rising bubbles can mix the pore water along the length of the tube, creating a sharp gradient immediately at the interface. Enhancement of diffusive transport consequently would result from the increased gradient.

The critical concentration at which bubbles form is dependent on hydrostatic pressure; thus, resistance to bubble formation increases with increasing depths (Hutchinson 1957). Gas ebullition generally occurs in shallow aquatic systems such as marshes and littoral zones, where surficial sediments are the site of intensive anaerobic metabolism. In hypereutrophic Wintergreen Lake, a shallow ($\bar{z} = 3.5$ m), hardwater lake in Michigan, Strayer and Tiedje (1978) measured an average methane ebullition rate of $21 \text{ mmol/m}^2\text{-d}$ during the period late May through August. Maximum rates of methane loss by bubble evolution ($35 \text{ mmol/m}^2\text{-d}$) occurred in late summer. In comparison, Martens and Klump (1980) measured an average methane ebullition of $16.8 \text{ mmol/m}^2\text{-d}$ from intertidal sediments on the North Carolina coast between June and October. Ebullition was initiated by the release of hydrostatic pressure that accompanied low tide. High fluxes of total dissolved phosphorus were observed; rates up to $120 \text{ umol/m}^2\text{-hr}$ were observed from these sediments during the summer months. The high rates were attributed to increased mass transport associated with bubble tubes maintained by methane gas ebullition.

Sediment Resuspension

A third mechanism that may contribute to internal loading is the resuspension of sediments in shallow lakes by wind-induced currents (e.g., Sheng and Lick 1979). Fee (1979) correlated rates of primary production in unfertilized ELA lakes in western Ontario to the fraction of epilimnetic surface area in direct contact with bottom sediments. Fee concluded that epilimnetic nutrient recycling is dominated by processes occurring at the sediment-water interface and not within the sediment. Chapra (1982) recently showed that resuspension becomes an important mechanism in lakes with mean depths less than 9.2 m. Lastein (1976) showed that approximately 24 percent of the material collected in sediment traps in Lake Esrom (Sweden) ($z = 12.3$ m) was from resuspended sediment, and he hypothesized that wind-induced circulation alone was sufficient to explain the phenomenon. In Lake Uttran (Sweden), a shallow ($\bar{z} = 5.7$ m), eutrophic lake, Ryding and Forsberg (1977) correlated aqueous total phosphorus concentrations with the force and duration of winds blowing lengthwise across the lake, and they suggested that resuspension played a dominant role in regulating water quality. In a study of six shallow Danish lakes, Andersen (1974) concluded that wind-induced mixing of surficial sediments is the most probable mechanism for the high phosphorus release rates he observed (up to $1.2 \text{ g/m}^2\text{-month}$). Concomitant laboratory studies indicated that maximum rates of release from quiescent, undisturbed sediments were of the order of $0.25 \text{ g/m}^2\text{-month}$.

Surface waves produce an oscillatory motion which translates in shallow water to elliptical orbits extending to the sediment-water

interface (Bascom 1964; U.S. Coastal Engineering Research Center 1977). Near the boundary layer, the elliptical motion is reduced to a simple, reciprocating horizontal motion, and the maximum horizontal velocity associated with the oscillating motion is given by

$$u_m = \frac{\pi H_s}{T_s \sinh(2\pi d / L_d)} \quad (I-1)$$

where H_s = significant wave height;
 T_s = significant wave period;
 d = depth of the water column;
 L_d = wavelength for the particular depth, d ; and
 u_m = maximum orbital velocity (Komar and Miller 1973).

When the shear force exceeds the bulk shear strength of the surficial sediment deposits, sediment resuspension occurs (Alishahi and Krone 1964; Komar and Miller 1973, 1975; Terwindt 1977; Sternberg 1972). Scour may be accomplished either by detachment and entrainment of individual flocs (surface erosion) or removal of aggregated material (mass erosion) (Lonsdale and Southard 1974; Terwindt 1977). In deposits where shear strength increases with depth, erosion continues to the depth where the applied stress is equivalent to the bed strength (Krone 1976). Below the threshold or critical shear velocity, the bed remains intact and no resuspension occurs. Migniot (1968) demonstrated that for various types of cohesive sediments, the critical shear velocity may be expressed as an inverse function of water content. These findings subsequently were confirmed for marine sediments by Southard et al. (1971) and Lonsdale and Southard (1974).

The critical shear velocity also is influenced by the mechanical structure of the sediment, which in turn is related to the solute characteristics and ionic strength of the interstitial solution and the eroding solution (Arulananden et al. 1975). For example, critical shear stress decreases with increasing sodium adsorption ratio (SAR) (Arulananden et al. 1975):

$$SAR = \frac{[Na^+]}{([Ca^{2+}] + [Mg^{2+}])^{1/2}} \quad (I-2)$$

This observation correlates with the Schulze-Hardy valence rule, which indicates that the critical coagulation concentration of mono-, di-, and trivalent ions are in the ratio of z^{-6} , where z is the charge of the ion (Stumm and Morgan 1981). Increasing the solute concentration of the pore fluid destabilizes colloidal suspensions (i.e., agglomerates them and tends to remove them from solution). The net effect is an increase in bed strength (Arulanandan et al. 1975). The effects of electrolyte concentration and SAR on critical shear stress and erosion rates were reviewed in detail by Terwindt (1977).

Mixing or agitation of surficial sediments due to wave action entrains interstitial (pore) water, resulting in release of solutes such as nitrogen and phosphorus species to the overlying water (Gahler 1969; Lam and Jaquet 1976). For example, resuspension of the upper 1 cm of a flocculent sediment with a porosity of 80 percent and a pore water phosphorus content of 1 mg/L would result in a release of 8 mg P/m². This is sufficient phosphorus to supply a shallow lake (e.g., $\bar{z} = 3$ m) with an additional 2.7 ug P/L from this source alone. In addition, a

substantial fraction of the inorganic phosphorus sorbed to lake sediments participates in rapid solid phase/aqueous phase exchange reactions. This reservoir of phosphorus may be more important in controlling the phosphorus flux resulting from sediment resuspension than is the pore water phosphorus.

Lam and Jaquet (1976) developed an empirical model to predict the upward flux of TP from resuspended sediment in Lake Erie. The flux is a function of shear stress at the sediment-water interface (τ_B) from wind-induced waves; τ_B was calculated from linear wave theory using the deep-water Sverdrup-Munk-Bretschneider (SMB) wave-hindcasting method to estimate wave height and period. Regeneration was assumed to arise primarily from organic and nonapatite inorganic phosphate fractions, in conjunction with a small quantity of soluble interstitial phosphate. Apatite $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ was not considered in the regeneration process because of its relatively high density and large grain size.

Sheng and Lick (1979) developed a similar sediment resuspension model for Lake Erie; a principal point of departure from the Lam and Jaquet model was the use of a shallow-water SMB wave-hindcasting model to predict bottom orbital velocities.

Molecular Diffusion

The existence of concentration gradients across the sediment-water interface implies that molecular diffusion may be an important mechanism in describing solute transport. Theoretically, the flux across the sediment-water interface constituent dissolved in the interstitial solution arises from advection due to pore water buried by sediment

deposition, as well as from diffusion (Imboden 1975; Lerman 1979).

Neglecting the advective component, the flux equation reduces to Fick's first law (Berner 1971):

$$J_s = - \phi_o D_s \left(\frac{\partial C}{\partial z} \right) \bigg|_{z=0} \quad (I-3)$$

where J_s = flux from the sediment to the overlying water
(g/cm²-s with "s" denoting bulk sediment),
 ϕ_o = porosity at the interface,
 D_s = bulk sediment diffusion coefficient at the interface
(cm²/s), and
 $\left(\frac{\partial C}{\partial z} \right)_{pw}$ = pore water (pw) concentration gradient at the
sediment-water interface (i.e., z=0).

This equation is tractable if the assumption is made that D_s is both spatially and temporally invariant. The flux of a dissolved species across the sediment-water interface then can be calculated from the concentration gradient at the interface and molecular diffusivity (e.g., McCaffrey et al. 1980; Thibodeaux 1979; Vanderborght et al. 1977).

Fluxes as high as 7 mg P/m²-d attributed to diffusion have been reported by Ulen (1978) for sediment cores from Lake Norvikken in central Sweden. The average diffusive flux for Lake Norvikken was 1.0 g/m²-y; this contrasts with an external phosphorus loading rate of 0.53 g/m²-y. Ulen (1978) obtained good agreement between empirically measured fluxes and calculated rates of exchange using a bulk sediment diffusion coefficient of 4.4×10^{-6} cm²/s. This value was first derived by Tessenow (1972) and probably represents an upper

limit for bulk sediment diffusivities (Tessenow 1972, in Kamp-Nielsen 1974). Data of Li and Gregory (1974) indicate that the diffusivities of H_2PO_4^- at 25°C and infinite dilution are $7.34 \times 10^{-6} \text{ cm}^2/\text{s}$ and $8.46 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively; Manheim (1970) suggested that these values are diminished by factors ranging from 0.05 to 0.5 in unconsolidated sediments, as a result of porosity and path tortuosity effects.

According to Kamp-Nielsen (1974), the aerobic release of phosphorus from sediments in Lake Esrom (Sweden) is controlled by both adsorption and diffusion. Berner (1976) modified the expression for Fickian diffusion to quantify the retarding influence of adsorption:

$$J_s = - \frac{D_s \phi}{1 + K} \left(\frac{\partial C}{\partial z} \right) \Big|_{z=0} \quad (\text{I-4})$$

where K = nondimensionalized linear adsorption coefficient.

Excellent agreement was obtained by Krom and Berner (1980b) between empirically-derived effective diffusivities for phosphate, ammonium, and sulfate ions and molecular diffusivities corrected for tortuosity and adsorption. The influence of adsorption on the effective or apparent diffusion coefficient can be quite significant; for example, Krom and Berner (1980a) cite values for K ranging up to 5,000 for oxic oceanic sediments.

Summary

Sediments in lakes are generally characterized by high concentrations of nutrient and other chemical constituents (such as heavy metals)

resulting from the deposition and accretion of detrital material. As a result, sediments may actively participate in regulating the cycling of a particular constituent in the water column. The extent that the sedimentary reservoir can ultimately influence material cycling within the water column depends on the availability of the substance for exchange. Exchange of nutrients and other solutes across the sediment-water interface into the overlying water is controlled by four principal mechanisms: bioturbation, gas ebullition, resuspension of bulk sediment by wind-induced turbulence, and molecular diffusion. In shallow lakes characterized by extensive fetches, sediment resuspension is likely to be a major mechanism for internal nutrient cycling. This research focuses on the significance of sediment resuspension on rates of internal nutrient release in two lacustrine systems of similar morphometry, but quite different trophic state--hypereutrophic Lake Apopka and mesotrophic Lake Okeechobee. In conjunction with this objective, a corollary objective of this study was to develop an event-dependent model to predict the release or removal of phosphorus by wind-induced sediment resuspension.

CHAPTER II

SITE DESCRIPTION AND METHODOLOGY

This research focused on two rather large and shallow lakes important as aquatic resources in Florida--Lake Apopka in central Florida and Lake Okeechobee in south Florida. By virtue of the broad fetch and shallow nature of each basin, both Lake Apopka and Lake Okeechobee are subjected to periodic sediment resuspension due to wind-induced currents. The trophic state of these two lakes, however, is quite different. Until the early to mid-1950's, Lake Apopka achieved national reknown as a bass fishing lake. Currently and primarily because of cultural inputs of nutrients, Lake Apopka is now widely regarded as one of the most eutrophic lakes in Florida. Conversely, Lake Okeechobee is intensively used as a recreational resource and is critical to the hydrologic and ecological stability of south Florida. The following section briefly summarizes the limnological characteristics of these two systems and details the specific analytical procedures used in this study.

Physical Description and Limnology of Lake Okeechobee

After the Laurentian Great Lakes, Lake Okeechobee is the largest freshwater lake in the United States. Located in south central Florida between latitudes 26°41' to 27°13'N and longitudes 80°36' to 81°07'W

(Figure II-1), Lake Okeechobee has a surface area of $1,890 \text{ km}^2$ at normal stage (approximately 4.6 m above sea level). The broadest expanse of open water lies along the north-south axis and approximates 56 km; the maximum east-west dimension is 48 km. The shoreline development index, which is the ratio of the lake shoreline length to the circumference of a circle with an equivalent surface area is 1.12 (Brezonik et al. 1979). Summarized in Table II-1 are some of the important physical characteristics of the watershed.

Lake Okeechobee, which is considered moderately eutrophic (Brezonik et al. 1979), is quite shallow throughout the entirety of its basin. At normal stage, the depth of the lake averages only 2.8 m and has a maximum depth of less than 5 m (Figure II-1). Because of its shallow depth, Lake Okeechobee is characterized by an extensive littoral zone. Macrophyte communities occupy nearly 500 km^2 or 26 percent of the total lake surface area along the southern and western shores of the lake; however, no important macrophyte communities are established on the eastern portion of the basin (Brezonik et al. 1979).

Lake Okeechobee in its present state originated approximately 6,000 years ago (Brooks 1974). It occupies a shallow depression which, according to Hutchinson (1957), was formed by epeirogenetic uplift of an irregular marine surface. Brooks (1974) has hypothesized that differential subsidence of the thick underlying sequence of Miocene clays is responsible for the deeper portions of the lake. Extensive discussions of the origin and early history of Lake Okeechobee have been presented by Brooks (1974) and Brezonik et al. (1979).

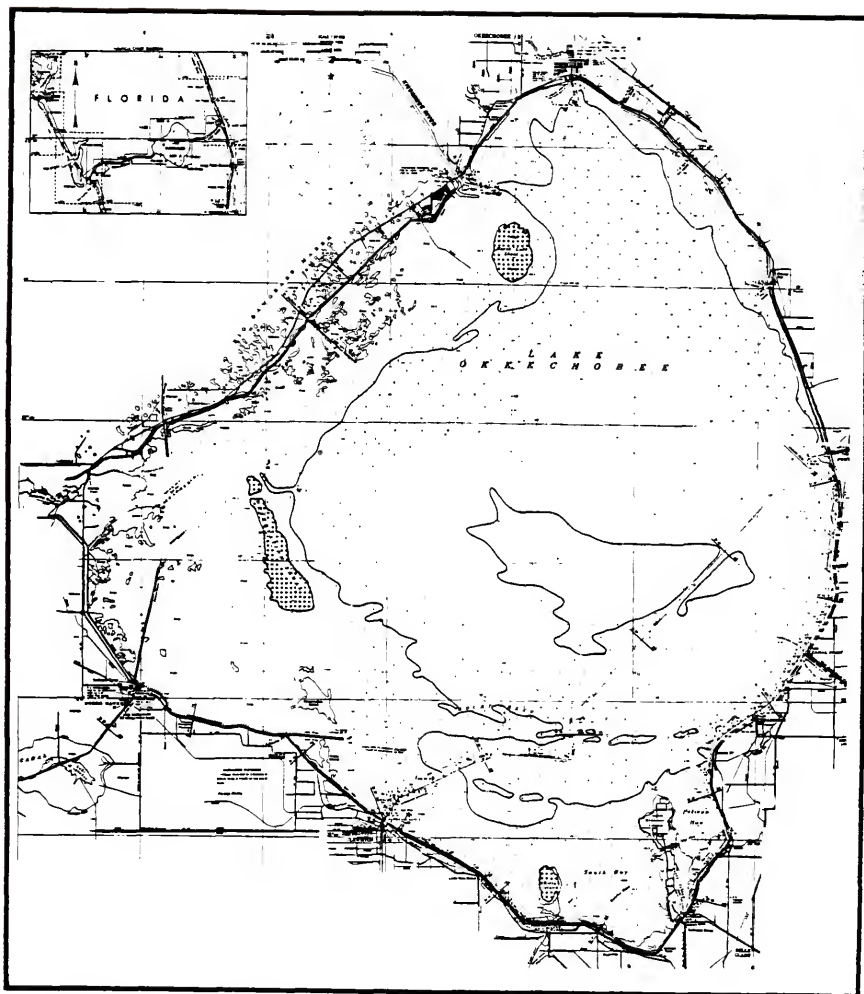


Figure II-1. Location Map of Lake Okeechobee.

Table II-1. Physical Characteristics of Lake Apopka and Lake Okeechobee.

	Lake Apopka*	Lake Okeechobee†
Lake Surface Area (km^2)	124.0	1,891
Maximum Depth, z_m (m)	11.0	4.7
Mean Depth, \bar{z} (m)	1.7	2.8
Volume, V (m^3)	2.14×10^8	5.24×10^9
Annual Inflow (m^3)	5.92×10^7	1.98×10^9 to 4.68×10^9
Theoretical Retention Time (years)	6.3	1.12 to 2.65
Maximum Length (km)	14.4	56.4
Maximum Width (km)	13.8	48
Shoreline Length (km)	58.5	172
Shoreline Development Index, D_L	1.48	1.13
Watershed Area (including lake) (km^2)	3.11	13,007
Watershed Land Area (km^2)	187	11,116

* From Brezonik et al. (1978).

† From Brezonik et al. (1979) and Federico et al. (1981).

Excluding the lake surface, the watershed of Lake Okeechobee drains approximately 11,116 km². The watershed comprises a series of both natural and man-made sub-drainage basins (Figure II-2). Flow is primarily from north to south; the Kissimmee River, which drains 6,048 km², is the most important tributary (Davis and Marshall 1975). Other natural basins of importance include Fisheating Creek (1,194 km²) and Taylor Creek which drain 1,194 and 477 km², respectively. Since the early 1900s, a 785 km² area of the Everglades immediately south of the lake has been added to the watershed via an extensive system of canal and pump stations. This region, otherwise known as the Everglades Agricultural Area (EAA), is dominated by Everglades muck soils and is intensively farmed. Flow in the EAA is conducted along the North New River, Hillsboro, and Miami and, depending on flood control and water conservation requirements, can be either imported from or exported to the lake. Hydraulic export from Lake Okeechobee is also conducted by the St. Lucie, West Palm Beach, and Caloosahatchee canals, whereas outflow historically occurred as sheet flow over the southern rim into the Everglades.

Land use within the Lake Okeechobee watershed has been compiled by McCaffrey et al. (1976). Results from the compilation are presented in Figure II-3 and Table II-2. In general, the watershed is dominated by some type of agricultural activity. Agricultural lands constitute 48 percent of the watershed and comprise primarily improved and unimproved pasture land in the northern and northwestern portions of the basin and croplands in the south. Wetlands are the next most significant land use type (18 percent), followed by surface water (18 percent

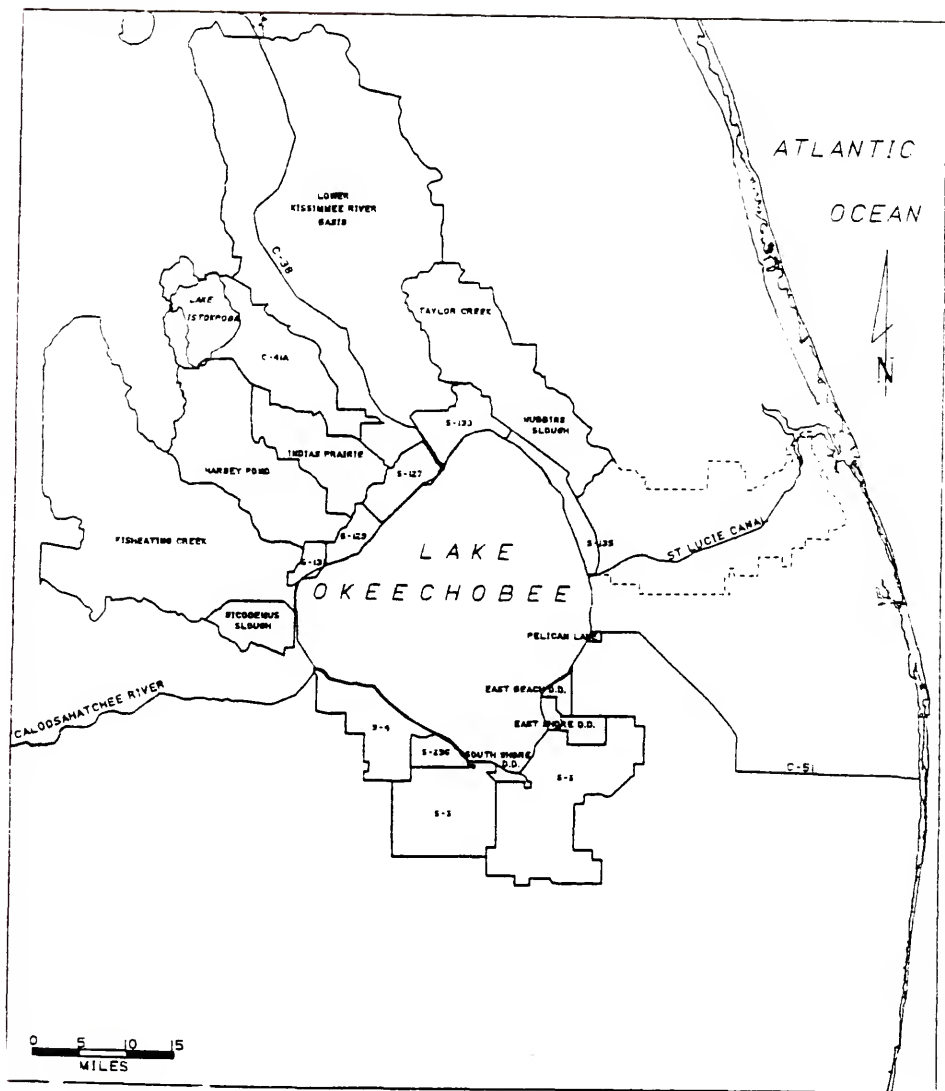


Figure II-2. Surface Water Drainage Basins in the Lake Okeechobee Watershed.

Note: Areas designated by dashed lines contribute only small amounts of water at irregular intervals. Drainage basins south of the lake have been added by man. From Federico et al. (1981).

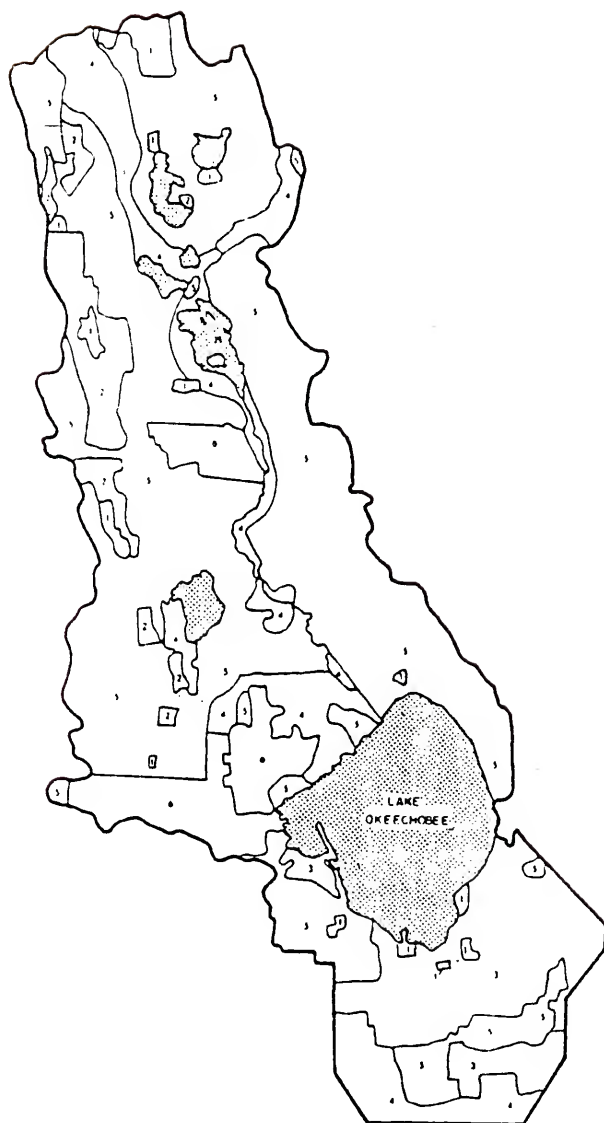


Figure II-3. Land Use Within the Lake Okeechobee Watershed. From McCaffrey et al. (1976).

Table II-2. Land Use within the Lake Okeechobee and Lake Apopka Watersheds (included are 1980 projections for Lake Okeechobee and 1990 projections for Lake Apopka).

Land Use	Lake Okechobee*				Lake Apopkat			
	1970		1980		1972		1990	
	Area (km ²)	Percent of Total	Area (km ²)	Percent of Total	Area (ha)	Percent of Total	Area (ha)	Percent of Total
Urban	623	4.0	813	5.3	1,578	5.1	3,035	9.8
Agricultural	7,636	49.5	7,442	48.1	17,118	55.0	15,661	50.4
Cropland	1,153	7.5	959	6.2	7,284	23.4	7,284	23.4
Citrus	688	4.4	660	4.2	8,094	26.0	8,094	26.0
Improved pasture	3,221	21.0	3,541	22.9	--	--	--	--
Unimproved pasture	2,570	16.7	2,286	14.8	1,740**	5.6	283**	0.9
Forest	870	5.6	935	6.1	--	--	--	--
Wetlands	2,865	18.5	2,813	18.2	--	--	--	--
Barren/Idle	708	4.6	700	4.5	--	--	--	--
Surface Water	2,756	17.8	2,756	17.8	12,400	39.9	12,400	39.9

* From McCaffrey et al. 1976.

† From ECFRRC 1973.

** Swamp and pasture.

including Lake Okeechobee) and forests (6 percent). Urban areas (5 percent), which include the towns of Clewiston, Belle Glade, and Okeechobee City, represent the smallest area of the total watershed.

Physical Description and Limnology of Lake Apopka

Lake Apopka is the fourth-largest lake in Florida, encompassing a surface area of 124 km². Located approximately 25 km northwest of Orlando between latitudes 28°33' to 28°41' and longitudes 81°31' to 81°42', Lake Apopka forms the headwaters of the Oklawaha chain of lakes, and ultimately the Oklawaha River (Figure II-4). As indicated by its shoreline development index (1.39), the lake is somewhat circular in shape and is characterized by relatively broad fetches extending along both the north-south and the east-west axes (14.4 and 13.8 km, respectively). Important physical characteristics of the watershed are summarized in Table II-1.

Lake Apopka resides at the southernmost end of the physiographic region known as the Central Valley, which is bounded on the west by the Lake Wales ridge and to the east by the Mount Dora Ridge. The lake itself occupies an extremely shallow basin with an average depth of only 1.7 m at normal stage (20.3 m above MSL) (Figure II-5); consequently, Lake Apopka is continually well mixed by wind-driven currents. Despite its shallow nature, the lake is characterized by the virtual non-existence of rooted macrophytes. This apparently stems from compression of the photic zone to much less than 1 m (approximately 40 to 60 cm) because of high algal densities characteristic of the hyper-eutrophic lake and the instability of the highly flocculent sediments.

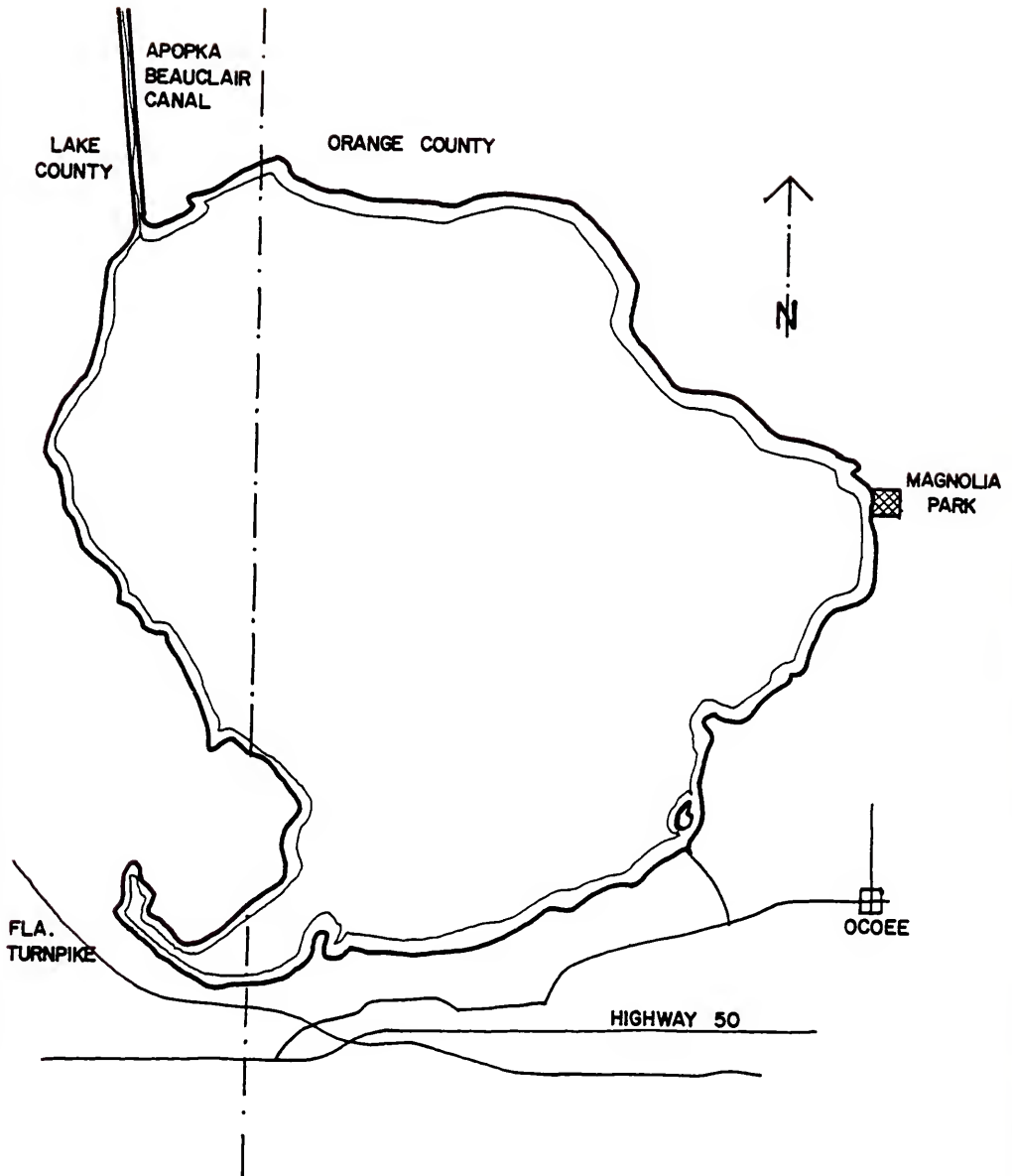


Figure II-4. Location Map of Lake Apopka.

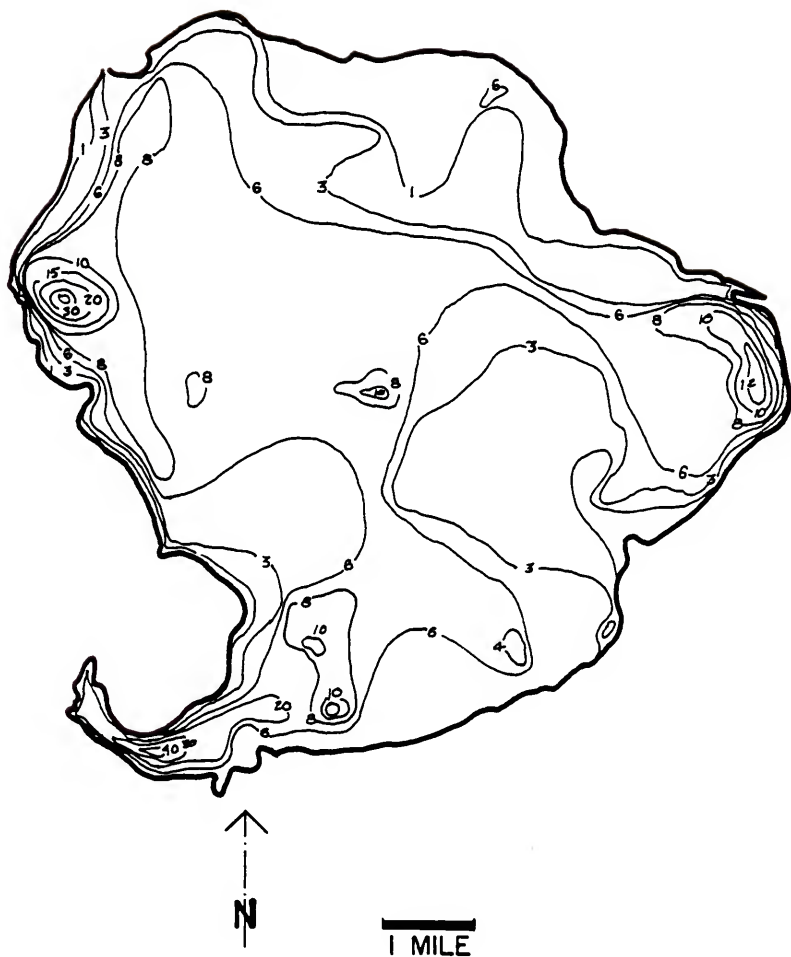


Figure II-5. Bathymetric Features of Lake Apopka. Depth Contours Given in Feet.

The watershed of Lake Apopka is rather small in relation to the lake surface area, and excluding the lake surface, drains only 187 km². No natural surface influents of any consequence convey water to the lake. The major hydraulic input is precipitation falling directly on the lake surface; the other important natural source is artesian flow from the Floridan Aquifer at Gourd Neck Springs in the southwest corner of the lake. During periods of intense rainfall, Johns Lake located 2.0 km to the south may overflow into Lake Apopka. Several other small streams in the southeastern basin Lake Apopka may flow into the lake; these streams are also ephemeral, and their existence is a function of antecedent rainfall.

Similar to Lake Okeechobee, the watershed of Lake Apopka has been increased by cultural activities. Around 1940, a vast (7,200 ha) marsh was drained and converted into highly productive muck farmland. Flow, which historically has been south to north, was diverted from the marsh by an earthen dike and conducted northward through the Apopka-Beauclair Canal. A series of canals and pump stations was constructed to regulate water level within the muck soils. As a result, backpumping for the for the muck farms has constituted a significant hydraulic (and nutrient) source; however, since 1976 the magnitude of this source has diminished considerably with the institution of discharge abatement measures.

Land use estimates within the Lake Apopka drainage basin have been developed by the East Central Florida Regional Planning Council (1973) and are included along with projections for 1990 in Table II-2. At the time of the above study, 8 percent of the land area was urbanized, while

citrus growing and muck farming activities occupied 43 and 39 percent of the land, respectively. As can be seen from Figure II-6, muck farming is limited to the northern perimeter of Lake Apopka, and most of the remaining land in the lake basin is occupied by citrus groves. Urban areas are primarily limited to sections on the south and west shores of the lake and include the towns of Winter Garden and Montverde.

Materials and Methods

Physical and Chemical Characterization

Samples were collected at 14 stations within Lake Okeechobee (Figure II-7) to determine physical and chemical characteristics of surficial sediments. Five stations (01, 03, 04, 08, 09) were located within the littoral zone; five stations (06, 07, 010, 011, 012) were open-water stations; and the remaining four stations (02, 05, 013, 014) may be described as transitional. Samples were collected during three sampling efforts in the summer and fall of 1980. Sediment samples from Lake Apopka were collected quarterly at nine open lake stations (A1 through A9) and one station at Gourd Neck Springs (A10) (Figure II-8) between March 1977 and March 1978. All samples were collected with a Ponar dredge and placed in wide-mouth one-liter polyethylene bottles, stored on ice until return to the laboratory and then refrigerated until analysis.

All sediment samples were homogenized prior to analysis. Water and volatile solids content were determined on a percent basis according to standard methods (APHA 1976). Particle size distribution was evaluated by wet sieve analysis for sand-sized fractions ($>63\text{ }\mu\text{m}$) and by pipette

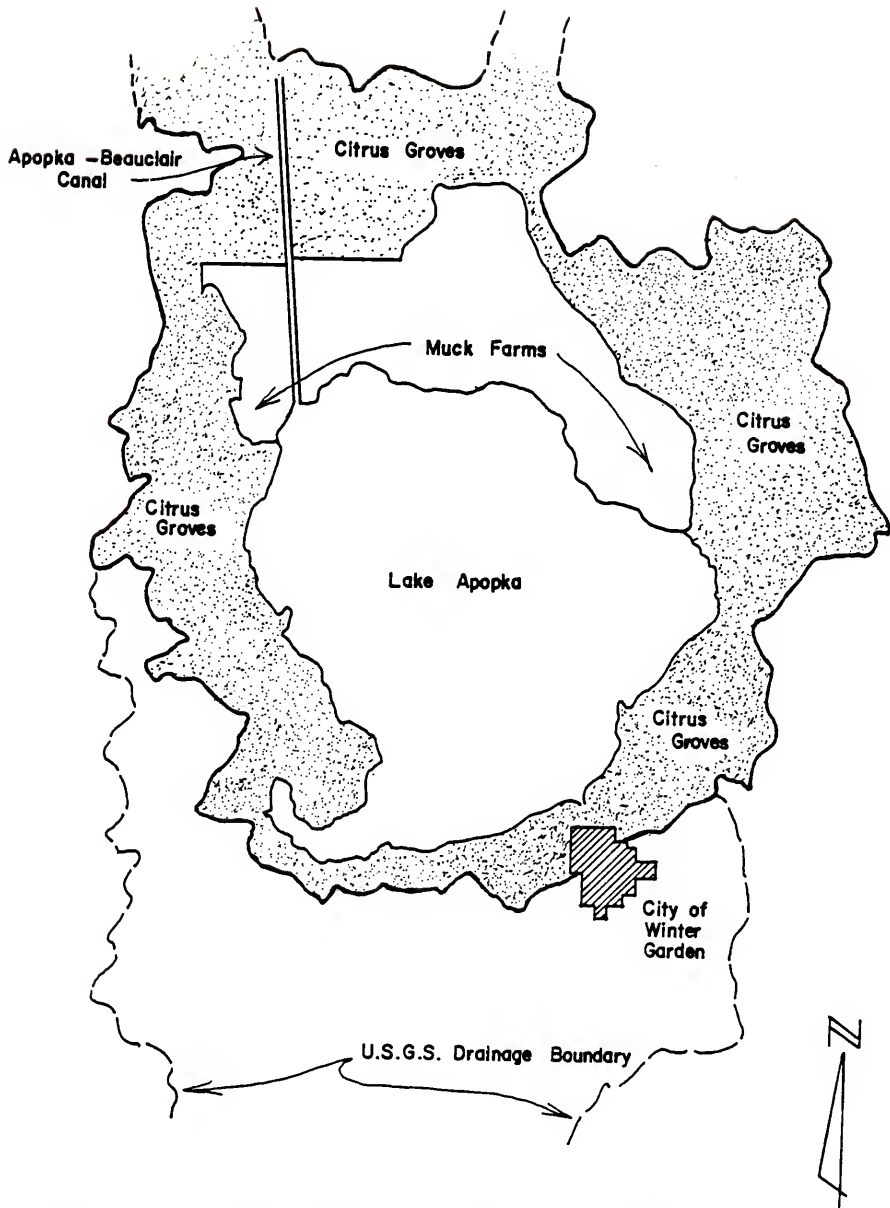


Figure II-6. Land Use Within the Lake Apopka Watershed.

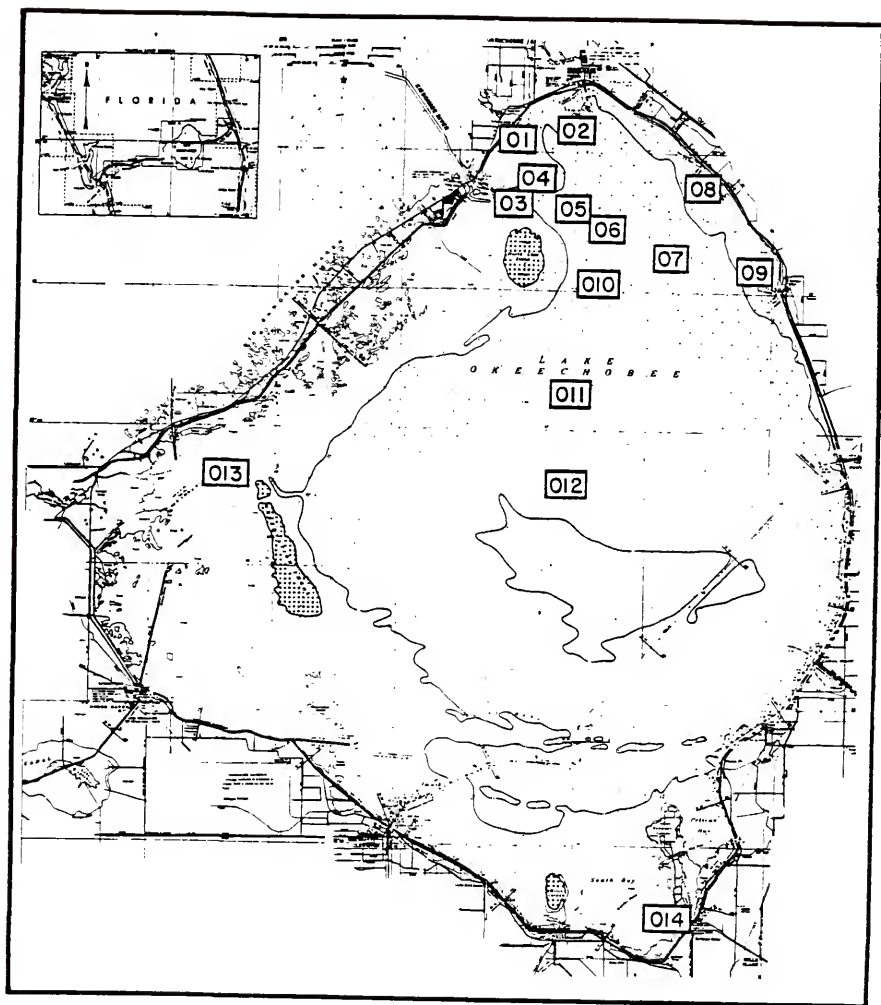


Figure II-7. Sediment Sampling Locations in Lake Okeechobee.

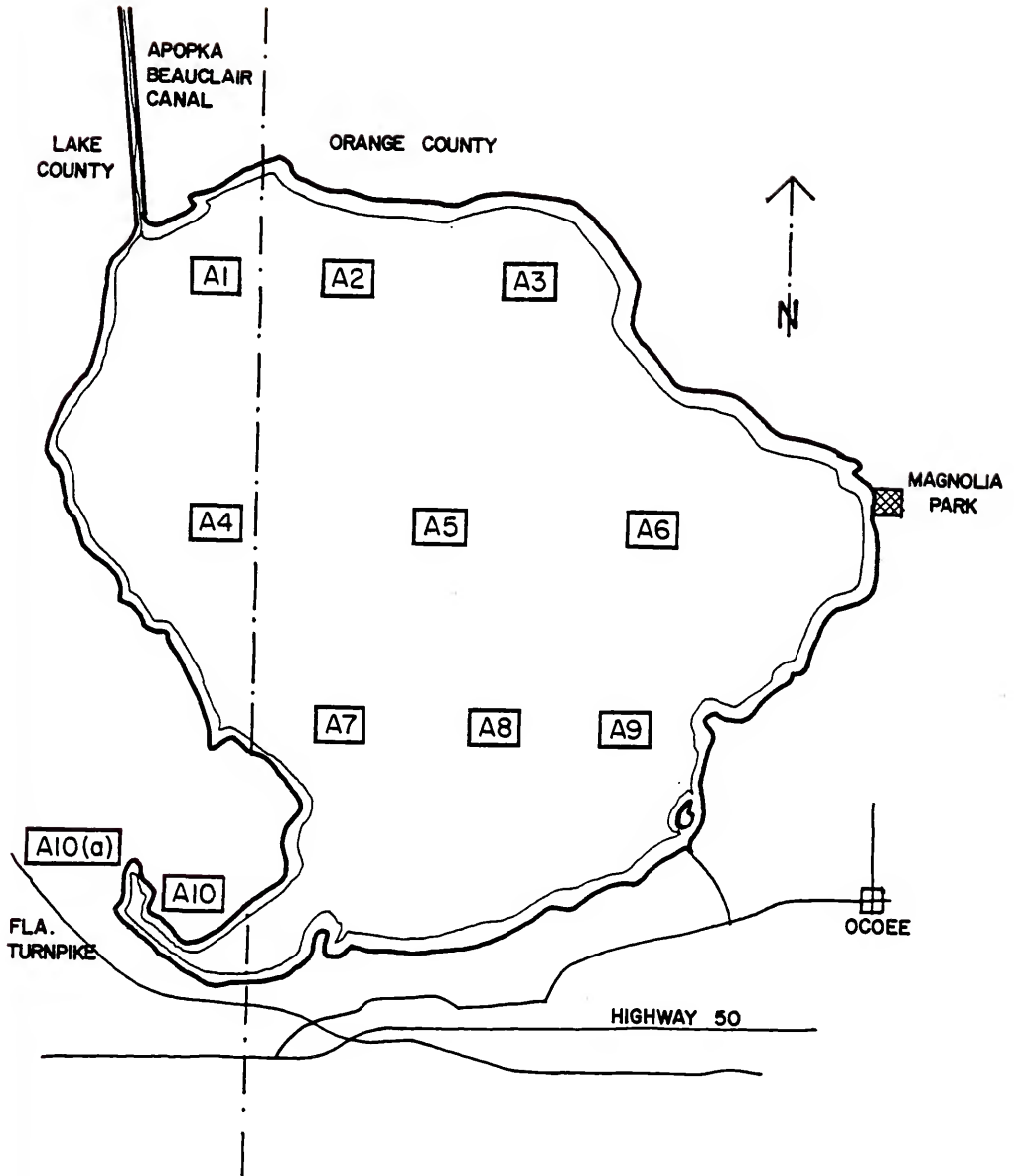


Figure II-8. Sediment Sampling Locations in Lake Apopka.

analysis for silt-clay fractions (Guy 1969). In order to characterize the effective particle size of the whole sediment, sedimentary organic matter was not removed by oxidation. Effective particle size is necessary in determining the threshold shear required to induce sediment resuspension for a particular sediment.

The phosphorus content of selected sediment samples was analyzed in terms of three fractions: apatite inorganic phosphorus (AI-P), nonapatite inorganic phosphorus (NAI-P), and organic phosphorus. The latter fraction was determined as the difference between the total phosphorus (TP) content and the sum of two inorganic fractions. The inorganic fractions were estimated on fresh (undried) sediments by the analytical method described by Armstrong (1979). This method involves a two-step sequential extraction scheme: the sample is initially extracted with 0.1 N NaOH for 16 hours to obtain NAI-P followed by an extraction with 1 N HCl for 16 hours to determine AI-P. TP was determined on fresh sediments by the acid-persulfate digestion technique (APHA 1976). Digested samples were filtered, neutralized, and analyzed for soluble reactive phosphorus (SRP) using the single reagent molybdenum blue technique (U.S. EPA 1976).

Interstitial water was extracted at 4°C by centrifugation of fresh sediment samples at 10,000 rpm for 30 minutes. The supernatant was then filtered through GF/C glass micro-fibre filter paper, and the filtrate was analyzed for SRP by the single reagent molybdenum blue technique (U.S. EPA 1976).

Sorption Experiments

A series of adsorption-desorption studies were conducted to quantify phosphorus exchange dynamics using sediment samples representative of littoral transitional and profundal zones. Sorption isotherms were evaluated at 22°C; samples were buffered at pH 8.3 with NaHCO_3 at an ionic strength of 8.5×10^{-3} M and 5.0×10^{-3} M. These conditions reflect the average pH and ionic strength observed in Lake Okeechobee (Federico et al. 1981) and Lake Apopka (Pollman et al. 1980), respectively. Aliquots of wet sediment equivalent to 0.5 g of oven-dried material were allowed to equilibrate with 100 mL of buffered water for 24 h on a rotary shaker table. The buffered solution was adjusted with KH_2PO_4 to yield initial orthophosphorus concentrations of 0, 20, 50, 100, 250, 500, 1,000, and 5,000 $\mu\text{g P/L}$. After 24 h of shaking, the suspensions were filtered through GF/C glass micro-fibre filter paper and subsequently analyzed colorimetrically for SRP using the method described previously. The quantity of phosphorus adsorbed or desorbed was determined from the difference between the final and initial concentrations and was corrected for contributions of SRP from interstitial water.

CHAPTER III PHYSICAL-CHEMICAL SEDIMENT CHARACTERISTICS

Physical Characteristics

Erosion, transportation, and deposition of sediment particles in a lake are governed by many physical factors, including effective fetch, water depth, bottom depth, and lake morphometry (Hakanson 1981). The sediment parameter that probably best indicates the dynamic conditions prevailing at the sediment-water interface is the water content of surficial sediment. For example, Migniot (1968) demonstrated an inverse relationship existed between critical shear stress and sediment water content for a series of lacustrine muds. Hakanson (1977) derived an empirical relationship that describes erosion and deposition of sediments in Lake Vanern (Sweden) as a function of sediment water content and maximum effective fetch (P_{eff}) (U.S. Coastal Engineering Research Center 1977). The water content of surficial sediments in Lakes Okeechobee and Apopka thus was determined to evaluate the physical nature of the sedimentary environment, i.e., whether a particular location within a lake basin is a zone of relative quiescence or an area subject to turbulence and resuspension.

Results for water content analyses for Lake Okeechobee and Lake Apopka are summarized in Tables III-1 and III-2, respectively. Sediments from the central portion of Lake Okeechobee had water contents ranging from 82.3 to 91.1 percent. With the exception of Station 09,

Table III-1. Summary of Physical and Chemical Characteristics of Lake Okeechobee Sediments.

Substrate Description Station	Approximate Depth, d (m)	Percent H ₂ O	Percent VS	Mean Particle Size (μ)	Interstitial P (mg P/L)	NAL-P (μ g P/g)	Apatite P (μ g P/g)	Total P (μ g P/g)
Pelagic								
06	2.6	89.15	15.31		0.003	14	29	502
010	2.4	91.07	12.66		0.004	12	12	--
011	3.4	82.28	17.21	270	0.002	35	349	527
012	3.4	85.16	33.41	170	0.075	39	564	995
07	3.4	83.16	35.05	59	0.012	66	783	1,440
Littoral								
09	0.6	71.52	14.98		0.148	43	74	248
08	1.1	42.32	1.18		0.004	8	17	407
01	0.6	58.28	1.44		0.008	9	54	142
03	0.9	45.68	2.74			24	158	284
04	0.8	52.21	3.48	208	0.267	30	199	388
Transition								
013	1.8	26.73	0.26	275	0.027	6	81	518
014	0.9	88.60	42.69	149	0.942	96	1,078	1,190
02	2.4	76.65	23.07	151	0.076	23	665	1,043
05	2.3	66.98	11.86		0.002	26	50	--

Table III-2. Summary of Physical and Chemical Characteristics of Lake Apopka Sediments.

Station	Approximate Depth, d (m)	Percent H ₂ O	Percent VS	Mean Particle Size (u)	Interstitial P (mg P/L)	NAI-P (ug P/g)	Total P (ug P/g)
A1	1.8	96.97	68.91		2.80		749
A2	0.9	96.58	55.96		0.40	83	902
A3	0.5	95.27	62.06	181	1.20		1,140
A4	1.8	96.07	63.35		1.90		1,100
A5	1.8	96.25	62.21	143	0.80	108	953
A6	1.8	96.32	65.01		1.70		1,020
A7	2.7	95.57	61.35		0.40		922
A8	1.5	96.88	61.69		0.70	111	1,170
A9	1.4	95.38	66.72		0.40		883
A10	12.2	95.08	77.38		0.40		1,320

the water content of littoral sediments within Lake Okeechobee was significantly lower ($p < 0.05$) than that of the central sediments and averaged only 49.6 percent. Station 09 was in the vicinity of beds of rooted macrophytes and emergent vegetation, which effectively dampen wave energy, thus permitting the accumulation of finer particles and detritus. Water content of sediments from transitional zones was quite variable, ranging from 26.7 to 88.6 percent, and reflected the gradation from a highly dynamic environment to more quiescent conditions. The difference between central-lake and littoral-zone sediments in Lake Okeechobee is further illustrated by the relationship between the fractional content of silt- and clay-sized particles and water content (Figure III-1). A close correlation ($r = .94$) was found between sediment water content and particle size distribution:

$$W = 41.16 + 12.66 (\ln B) \quad (\text{III-1})$$

where W = percent water content, and

B = cumulative mass percent (sediment particles $< 63 \mu\text{m}$ in diameter).

Thus, the near-shore sediments within Lake Okeechobee tend to be large grained with low water content, while the central-lake sediments are fine grained with high water content. A similar relationship for Lakes Vanern and Ekoln (Sweden) was derived by Hakanson (1977), who approximated water content as a function of mean particle size. In general, water content (or more specifically porosity) increases with decreasing particle size, as a result of increasingly effective electrostatic (repulsive) forces between clay minerals (Berner 1971, 1980).

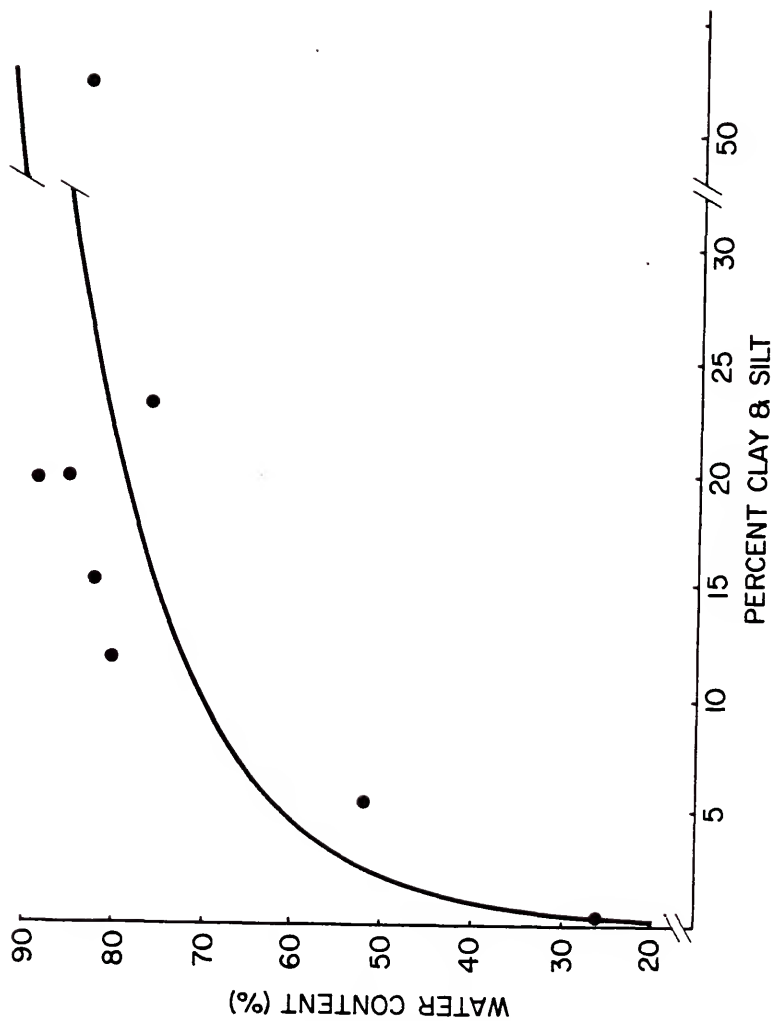


Figure III-1. Relationship Between Water Content and Fractional Silt-Clay Content for Surficial Lake Okeechobee Sediments.

In contrast to Lake Okeechobee, the sediments of Lake Apopka are relatively homogeneous with respect to water content; this trend implies a somewhat uniform hydrodynamic environment. Lake Apopka is characterized by extensive deposits of highly flocculent sediments with water content ranging between 95.1 to 97.0 percent. According to Schneider and Little (1969), these unconsolidated deposits cover 90 percent of the lake bottom with an average thickness of 1.5 m. Excluding the immediate shoreline, stable sediments comprising sand and shells are restricted to four small areas. The largest of these areas is a 240-ha region in the northern portion of the lake basin; the second largest region encompasses 120 ha adjacent to Crown Point near the eastern shoreline.

Sly (1978) suggested a simple approach to evaluate the occurrence of sediment suspension. According to Sly, the depth at which wave-induced shear stress exceeds the critical shear stress (τ_c) of bed materials corresponds to 25 percent of the available wavelength (based on significant wave period). For Lake Okeechobee, the deepest portion of the basin is approximately 4.3 m deep and has a maximum fetch of 20 km. Applying linear wave theory (U.S. Coastal Engineering Research Center 1977) to Sly's (1978) model, one calculates that sediment transport can be initiated in the deepest part of Lake Okeechobee at continuous wind velocities of 13.1 m/s (29 mph) or greater. It is thus apparent that sediment erosion and transport can be induced throughout Lake Okeechobee and that sediment accumulation tends to be restricted to relatively protected areas along the southern edge of the main basin (South and Pelican Bays) and the subbasin in the northern portion of the lake. The relatively low water content (<90 percent)

generally observed throughout the lake and especially in the deeper portion are indicative of substantial wave energy extending to the sediment surface. For example, according to Hakanson's (1981) model for sediment transport, sediments at a depth of 1 m in accumulating regions of Lake Okeechobee should exhibit water contents exceeding 80 percent. In Hakanson's model, the critical water content defining the limit between sediment transport and accumulation was found empirically to approximate

$$W_c = W_{\max} - 10 \quad (\text{III-2})$$

where W_c = the critical water content, and
 W_{\max} = the water content at the maximum depth.

Of the three samples collected at this approximate depth (Stations 03, 08, and 014) only Station 014 located within South Bay had a water content suggesting active sediment deposition. Despite the expansive fetch that extends to South Bay during wind events from the north (nearly 58 km), South Bay apparently is sufficiently sheltered by Rocky Reef, macrophyte vegetation, and by the shoreline configuration to serve as a settling basin. Moreover, prevailing winds originate from the east, resulting in more limited fetches for South and Pelican Bays.

According to Hakanson's (1981) model, the only other station within Lake Okeechobee with sediment water content indicative of relatively undisturbed accumulation is Station 09, which is located within a protective stand of rooted macrophytes. The central (open-lake) stations experience a mixture of deposition and erosion, resulting in

the accumulation of silt- to sand-sized particles (Table III-1). In shallow lakes such as Lake Okeechobee, continued circulation and upwelling prevent deposition of extremely fine particles, as Sly's (1978) model predicts.

Excluding several relatively deep and narrow trenches along the western and southern shores (4.9 and 5.5 m, respectively), the deepest portion of the major basin of Lake Apopka is only 3.0 m in depth and has an effective fetch of 7.4 km for winds originating from the east. Under these conditions, Sly's (1978) model indicates that resuspension can be initiated at wind velocities of 9.4 m/s (21 mph) or greater. This result suggests the ease with which sediment resuspension occurs in Lake Apopka. Because of its morphometry, quiescent regions of undisturbed deposition are essentially nonexistent. Indeed the water column of Lake Apopka often assumes a brownish cast because of wind-induced scouring of the bottom sediments; for example, turbidities in Lake Apopka often exceed 40 NTU (cf. Brezonik et al. 1978, 1981; Tuschall et al. 1979; and Pollman et al. 1980) and have been observed as high as 120 NTU (see Chapter IV).

Use of Sly's (1978) model as a guideline indicates that virtually the entire basin of Lake Apopka is subjected to resuspension; the only regions falling outside Sly's (1978) threshold criterion are the previously mentioned trenches along the western and south shores and the relatively protected subbasins comprising Gourd Neck Springs. Given the extremely flocculent nature of the sediments, the existence of such trenches is unusual. Bush (1974) explained their existence as a result of scouring created by wave setup. Wind-induced surface currents are

maximized along the longest reaches of a lake, resulting in a piling-up of surface water toward the leeward shore. The pressure thus exerted induces a return flow along the bottom in the opposite direction, scouring the bottom of muck.

These results conflict with a priori conceptions concerning sediment water content and lake hydrodynamics. The consistent and extremely high water content of Lake Apopka sediments suggests (in the absence of other information) that quiescent conditions prevail throughout the basin. A similar conclusion is reached from Hakanson's (1981) model, which indicates that water contents in excess of 90 percent reflect an undisturbed depositional environment. It is apparent from the previous discussion of Sly's (1978) model that the morphometry of the Apopka basin precludes undisturbed deposition. The question then arises as to why such high sediment water contents are observed throughout Lake Apopka.

Lake Apopka, by virtue of its shallow nature and inherently high rates of algal productivity, constitutes a rather unique depositional environment that falls beyond the framework of Hakanson's (1981) model. Average rates of net primary production as high as $465 \text{ mg C/m}^3\text{-hr}$ have been observed for Lake Apopka, with an annual average rate of $140 \text{ mg C/m}^3\text{-hr}$ reported by Brezonik et al. (1978). Compared with the threshold level of $95 \text{ mg C/m}^3\text{-hr}$ reported by Brezonik and Shannon (1971) for eutrophic lakes, these results show that Lake Apopka is highly eutrophic. As evidenced by sedimentary concentrations of volatile solids, high rates of deposition of organic detritus are a direct consequence of high rates of algal production. Average sedimentary organic content (as defined by volatile solids) ranged between 56.0

and 77.4 percent in Lake Apopka, and the lakewide average was 64.5 percent. Organic detritus, which has a bulk density approaching water, is readily resuspended and transported by wind-induced currents, and its accumulation in sedimentary deposits generally reflects not only rates of biogenic material production but also the vertical distribution of hydrodynamic forces. In most lakes, then, transitional hydrodynamic environments occur that result in selective deposition of particles as a function of size and density. Consequently, sediment-focusing or high rates of deposition of organic-rich material are observed in the deeper reaches of these systems (cf. Davis and Ford 1982). However, because of the configuration of Lake Apopka's basin, relatively undisturbed depositional zones are non-existent. Consequently, a virtually uniform layer of highly flocculent, organic sediments prevails throughout the basin.

Unlike Lake Apopka, the distribution of organic material in Lake Okeechobee clearly demonstrates a transitional hydrodynamic environment. Organic content varied with station location in the basin, ranging from 0.3 to 42.7 percent (dry weight) (Table III-1). Sediments in littoral areas (excluding Station 09) exhibited very low concentrations of organic matter, averaging only 2.2 percent. Organic content of open-lake sediments was significantly higher and ranged between 12.7 and 35.1 percent.

Two classes of open-lake sediments in Lake Okeechobee can be identified from the results of this study. The first class consists of highly organic muck (Stations 07 and 012), with sediment organic content approximately 34 percent. These sediments tend to predominate in the

mid to north central portion of the lake basin. The second sediment association, which occurred at Stations 06, 010, and 011, is less organic in nature, averaging 15.1 percent, and was found in closer proximity to the shoals of the western basin. Sediment organic content was highest at Station 014 in South Bay, with organic matter constituting 43.2 percent of the total solid content. South Bay, which previously was identified as a settling basin, receives substantial portions of inorganic nutrients from the Everglades Agricultural Area (Federico et al. 1981).

Further evidence supporting the idea that detrital accumulation in Lake Okeechobee is influenced by hydrodynamic factors is supplied by evaluating the relationship between organic matter and water content in Lake Okeechobee sediments. A logarithmic correlation ($r = .92$) was observed between water content and organic content (Figure III-2):

$$W = 43.21 + 12.37 (\ln VS) \quad (III-3)$$

where VS = percent volatile solids dry weight.

A similar logarithmic relationship was noted by Nisson (1975) for sediments from Lakes Harney, Jessup, and Monroe, on the St. Johns River in central Florida.

If detrital accretion in sediments primarily reflects hydrodynamic factors, a correlation also should be observed between particle size and organic content. This relationship stems from the fact that the conditions that favor the deposition of fine-grained sediments are also conducive for the accretion of detritus. For sediments in Lake

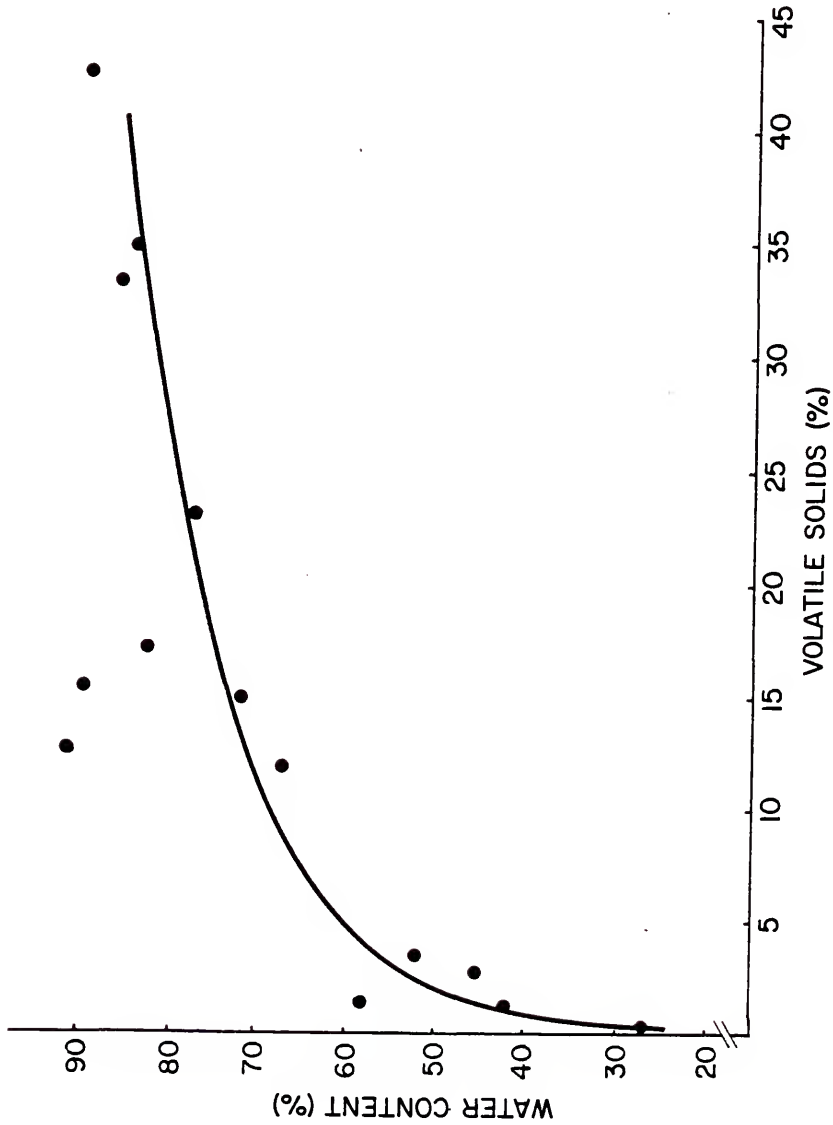


Figure III-2. Relationship Between Sediment Water Content and Organic Content Expressed as Volatile Solids for Surficial Lake Okeechobee Sediments.

Okeechobee containing 23 percent organic matter or less, this is indeed the case (Figure III-3). In this range, organic content and silt-clay content are linearly related. With organic content exceeding about 23 percent, however, the fractional silt-clay content remains constant (approximately 20 percent), suggesting that in quiescent waters localized rates of primary production assume a greater role in controlling the magnitude of detrital deposition. The fractional silt-clay and organic content of Station 06 does not conform to this relationship; unique morphometric and hydrodynamic factors may permit greater deposition rates of colloidal silt-sized particles at this site.

Chemical Characteristics

The chemical nature of sedimentary phosphorus defines its availability for exchange and biological uptake. Differential dissolution schemes have been developed that correlate algal availability with a particular fraction. Such fractionation schemes were applied to Lake Okeechobee and Lake Apopka sediments, and results are described in this section. Total P analyses, on the other hand, provide an estimate of the total pool of phosphorus that ultimately is available for exchange.

Total phosphorus (TP) concentrations in Lake Okeechobee sediments were highly variable and ranged from only 142 ug P/g (dry weight) to 1,440 ug P/g. Conversely, the distribution of TP in Lake Apopka sediments was fairly homogeneous and reflects the uniformity of the depositional environment in the lake. Concentrations in sediments within the main basin ranged from 749 ug P/g at Station A1 to 1,170 ug P/g at Station A8. TP concentrations in Station A10 sediments at Gourd

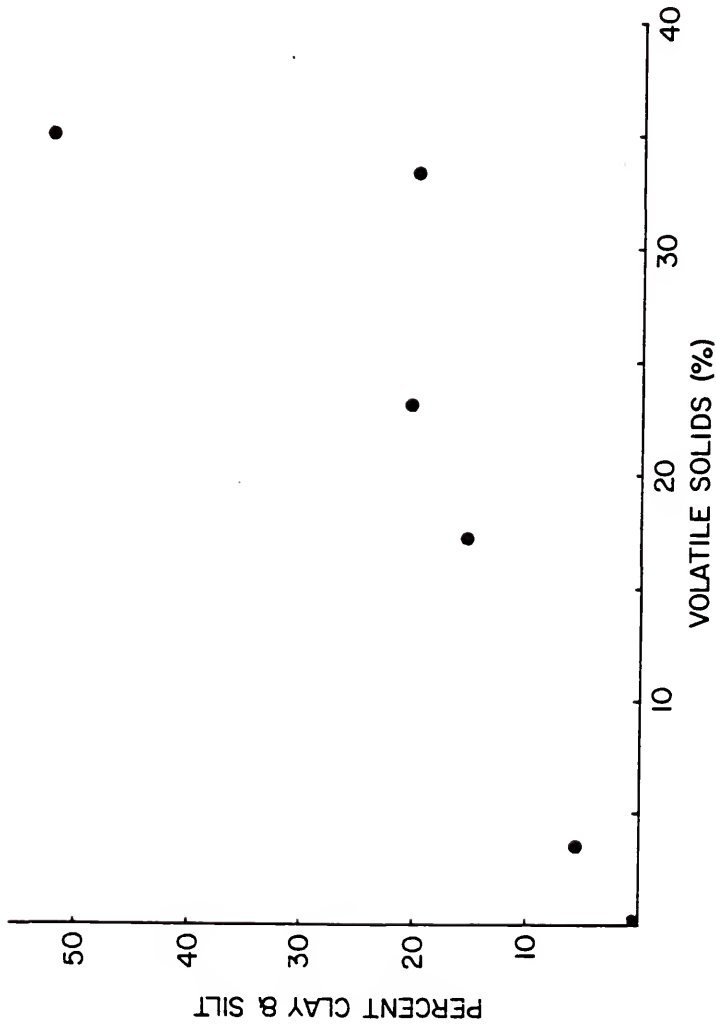


Figure III-3. Relationship Between Fractional Silt-Clay Content and Organic Content Expressed as Volatile Solids for Surficial Lake Okeechobee Sediments.

Neck Springs were somewhat higher (1,320 ug P/g) because of the deposition of large quantities of decaying water hyacinths (Eichornia crassipes). Phosphorus concentrations in lacustrine sediments may range as high as 7,500 ug P/g, but typically are less than 2,500 ug P/g (Jones and Bowser 1978). In a survey of mineralogical constituents comprising profundal Minnesota lake sediments, Dean and Gorham (1976) observed an average TP concentration of 1,400 ug P/g in calcareous lakes. Although it is apparent that TP concentrations in Lake Okeechobee and Lake Apopka sediments fall somewhat within the lower end of the spectrum, the observed concentrations approach and in some cases exceed the 1,000 ug P/g threshold level cited by Frink (1967) as indicative of eutrophication.

Within Lake Okeechobee, the highest TP concentrations generally were observed in the pelagic reaches of the lake basin. TP concentrations in pelagic sediments ranged from 502 to 1,440 ug P/g with an average value of 866 ug P/g; concentrations in littoral sediments were significantly lower ($p < 0.05$), averaging only 294 ug P/g. These results imply that selective size sorting processes influence sedimentary P distribution; similar results have been reported by Frink (1967 and 1969) and Hakanson (1981), as well as others. Based on the relatively poor correlation between water content and TP in Lake Hjalmarén sediments ($r = .68$), however, Hakanson (1981) concluded that accretion of sedimentary P is mediated by anthropogenic and/or chemical factors in addition to hydrodynamic processes. The weak correlation ($r = .57$, Table III-3) between TP and water content in Lake Okeechobee sediments implies a similar conclusion.

Table III-3. Summary of Sedimentary Component Interrelationships with Total Phosphorus Concentrations in Lake Okeechobee Sediments.

Relationship	r^2
NAI-P vs. TP	.46
AI-P vs. TP	.81
Interstitial SRP vs. TP	.19
Volatile Solids vs. TP	.76
Water Content vs. TP	.32

As indicated by linear regression analysis, the accumulation of sedimentary P in Lake Okeechobee is dictated to a significant extent ($p < 0.05$) by the deposition of apatite-inorganic P (AI-P) (Table III-3). With the exception of organic content, correlations between TP and other sediment parameters were weak and insignificant at the 95 percent confidence level.

Mechanistically, the functional dependency of sediment TP content on AI-P and organic content may be explained by evaluating the relationship between calcium-carbonate solubility, calcium-phosphate solubility, and pH changes induced by primary production. The premise of this hypothesis is that deposition of AI-P and detrital material are causally linked to the same forcing function--primary production. For example, calcium carbonate precipitation may be induced by increases in pH that result from net primary production (Kelts and Hsu 1978); calcite surfaces act as heterogeneous nuclei for calcium phosphate minerals (Stumm and Leckie 1971; Griffin and Jurinak 1973), resulting in removal of phosphorus from the water column. Similarly, calcium-phosphate minerals tend to become less soluble with increasing pH (within the range for most natural waters) owing to a shift in phosphorus speciation and, in the case of hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, an increase in hydroxide concentration. To test the hypothesis that AI-P deposition may be influenced by biogenically induced pH shifts, the stability of various calcium phosphate mineral phases in Lake Okeechobee was evaluated by comparing measured ion activity products (IAP) for the species with thermodynamic solubility products (K_{s0} values). For purposes of this exercise, two pH values were used: 8.10, the average

pH and 9.10, the maximum pH observed by Federico et al. (1981) for a series of stations near South Bay. Reported average Ca concentrations approximated 46.5 mg/L. Average orthophosphorus concentrations at these stations ranged between 0.020 mg P/L and 0.025 mg P/L; for the purposes of this exercise a concentration of 0.0225 mg P/L was assumed. Of the three mineral phases evaluated [CaHPO_4 , $\text{Ca}_4\text{H}(\text{PO}_4)_3$, and hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$], only hydroxyapatite is stable under ambient conditions in Lake Okeechobee (see Table III-4). During periods of high photosynthetic activity (i.e., high pH), the water column is greatly supersaturated with respect to hydroxyapatite ($\text{IAP}/K_{\text{sp}} > 10^8$), and this may result in the direct precipitation and subsequent incorporation of this species in the sediments.

Similar relationships between sedimentary TP and sediment inorganic P were observed by Wildung et al. (1974) in Upper Klamath Lake, a non-calcareous lake located in Oregon. Unfortunately, inorganic P as reported by Wildung et al. (1974) includes both non-apatite inorganic P (NAI-P) and as AI-P, thus precluding a direct comparison of results. In direct contrast to the results of this study, however, Williams et al. (1980) found a weak, negative correlation between TP and AI-P in sedimentary material derived the drainage basins of Lakes Ontario and Erie. Williams et al. (1980) demonstrated strong correlations between variability in TP concentrations and changes in both NAI-P and organic P fractions; in Lake Okeechobee sediments, however, neither parameter yielded a significant ($p < 0.05$) correlation with sediment TP.

NAI-P, which is indicative of the sedimentary P reservoir directly available to algae upon resuspension (Williams et al. 1980; Allan et al.

Table III-4. Solubility Product Constants (K_{s0}) and Calculated Ion Activity Products (IAP) for Several Calcium Phosphate Mineral Phases as a Function of Ambient Ca (1.16×10^{-3} M), SRP (7.26×10^{-7} M), and pH Levels in Lake Okeechobee.

Solid Phase	log K_{s0} *	pH 8.10		pH 9.10	
		log IAP	log (IAP/ K_{s0})	log IAP	log (IAP/ K_{s0})
CaHPO_4	-6.6	-10.1	-3.5	-10.1	-3.5
$\text{Ca}_4\text{H}(\text{PO}_4)_3$	-46.9	-55.1	-8.2	-54.9	-8.0
$\text{Ca}(\text{PO}_4)_6(\text{OH})_2$	-114	-111.6	2.4	-105.4	8.6

* From Stumm and Morgan (1981).

1980), generally is low in Lake Okeechobee sediments. Concentrations ranged from 6 to 96 ug P/g and generally constituted less than 9.0 percent of the total P content. From vertical profiles of nutrients in Lake Okeechobee sediment cores Brezonik et al. (1981) inferred a sediment suspension or bioturbation depth of 10 cm; for Station 07 sediments this implies a labile P pool of approximately 1.04 g P/m^2 which is sufficient to increase existing levels by 305 ug P/L (of labile P) if the entire reservoir was released in a single pulse event. Despite the relatively low concentrations of NAI-P, this calculation illustrates the inherent potential for photosynthetic stimulation induced by nutrient exchange across the sediment water interface.

Concentrations of NAI-P in Lake Apopka sediment were relatively uniform and ranged from 83 to 111 ug P/g. Similar to Lake Okeechobee, this fraction comprises only 10 percent of the total P reservoir. However, the inherent potential for this reservoir to support primary production in the water column is considerable. For example, at Station A5 with average NAI-P and interstitial SRP concentrations of 108 ug P/g and 0.80 mg P/L, respectively, the total potential release of inorganic phosphorus to the water column by resuspending only 1 cm of sediment is 49 mg P/m^2 . This is equivalent to an incremental addition of 29 ug P/L to the water column. Of this total, the NAI-P fraction contributes about 84 percent. It is important to note that resuspension of sediment to a depth of 4.7 cm has been observed in Lake Apopka during convective disturbances (see Chapter IV) and most likely extends more deeply into the sediment.

The distribution of SRP concentrations in sediment pore fluids for both Lake Okeechobee and Lake Apopka was somewhat erratic, and no trends were discernible between sediment type and interstitial SRP. Interstitial SRP concentrations in Lake Apopka were quite high and ranged from 0.40 to 2.80 mg P/L. The source of this variability is apparently a combination of physical, biological, and chemical factors. For example, the ability of Lake Apopka sediments to further adsorb phosphorus (and hence buffer interstitial SRP concentrations within a relatively narrow concentration range) is virtually exhausted and is limited to extremely high concentrations. Under these conditions, small changes in the concentration of phosphorus adsorbed to sediment particle surfaces can result in very large changes in equilibrium SRP concentrations in the pore fluid (see Chapter V). In addition, interstitial SRP levels increase as organic phosphorus is mineralized by microbial heterotrophs. Pore fluid concentrations apparently continue to increase until the sediments are disturbed and this pool is exchanged with the overlying water. The sediments then reequilibrate at a lower but still highly elevated (relative to the water column) concentration.

Interstitial SRP concentrations in Lake Okeechobee sediments ranged from 0.002 mg P/L to 0.942 mg P/L with the maximum concentration found in the nutrient-enriched, highly organic sediments of Station 014. On the other hand, the pore water content of SRP in Station 07 sediments, which also were quite organic, was only 0.012 mg P/L, and the interstitial SRP content of the relatively inorganic, sandy sediments of Station 04 was substantially higher (0.267 mg P/L). Despite the variability in concentrations, it is clear that SRP concentrations in

the interstitial fluids were generally quite low, and this fraction constitutes less than 0.1 percent of the total sedimentary P. The ability of calcareous sediments (and specifically calcium carbonate) to adsorb P is well documented (e.g., Griffin and Jurinak 1973 and 1974), and Morse and Cook (1978) suggested that this mechanism accounts for the low levels of dissolved interstitial SRP found in carbonate-rich marine sediments. The small size of the interstitial reservoir implies that this pool is not a significant source of phosphorus to the overlying water via advective exchange across the interface. For example, resuspension of 10 cm of sediments from Station 07 would result in addition of only 0.3 ug P/L to the water from entrained pore water.

CHAPTER IV RELEASE STUDIES

A series of passive exchange studies were conducted to evaluate P release over a broad range of water content for Lake Apopka sediment. Sediment was collected from Station A2 and placed in five small aquaria with surface areas approximately 305 cm². Aquaria were filled with fresh sediment to a depth of approximately 13 cm and were exposed to varying intensities of artificial light from two 150 watt spotlights to generate a gradient of sediment dessication. Initial water content was 95.1 percent, final values ranged from 13.8 to 88.3 percent (Table IV-1). As dessication proceeded, surface areas decreased correspondingly and ranged from reductions of 18.5 to 78.9 percent. Following dessication, the aquaria were refilled with phosphorus-free 6.0×10^{-4} M CaCO₃ to simulate ambient alkalinities observed in Lake Apopka and were allowed to remain quiescent for a 9-day period. Samples of the overlying water were taken on a daily basis to determine the quantity of SRP released.

Phosphorus release by simple diffusion is illustrated in Figure IV-1. The appropriate theoretical (Fickian) expression for describing the flux of phosphorus across the sediment-water interface is given by the solution to Fick's first law of diffusion:

$$J = \phi D_s \frac{dC}{dz} \quad (\text{IV-1})$$

Table IV-1. Final Volatile Solids and Water Content of Partially Dessicated Lake Apopka Sediments Used in Passive Exchange Experiments.

Aquarium	Water Content (percent)	Volatile Solids (percent)
1	88.30	69.99
2	86.18	70.58
3	34.31	68.58
4	13.87	70.90
5	13.82	70.94

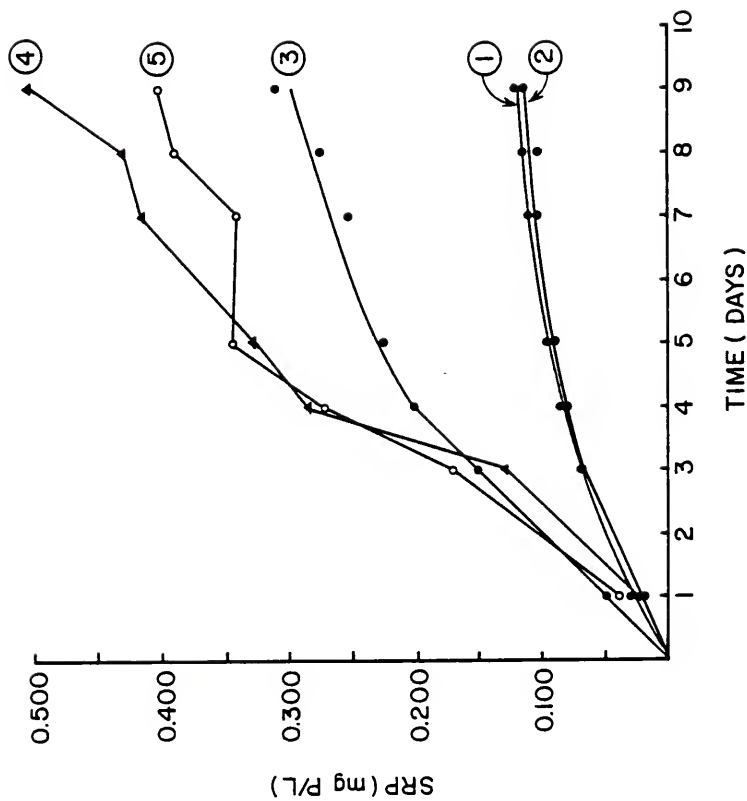


Figure IV-1. Passive (Diffusive) Release of SRP by Partially Desiccated Lake Apopka Sediments (Station A2) with Time. Release Studies were Conducted at Various Levels of Desiccation Designated by Graph Number. See Table IV-1 for Water Content Concentrations.

where J = flux of phosphorus across the interface ($\text{g P/cm}^2\text{-s}$),

\emptyset = porosity of the sediment (dimensionless),

D_s = the whole sediment diffusion coefficient ($\text{cm}^2\text{-s}$),
and

$\frac{dC}{dz}$ = the concentration gradient at the interface (g/cm^4).

This simple model assumes that the flux across the interface is strictly due to molecular diffusion and that deposition or compaction of sediment particles is negligible (cf. Lerman 1979; Berner 1981). The change in concentration in the water column at any particular point in time is simply the flux across the interface divided by the depth of the water column; this of course assumes that the water column is well mixed and is a reasonable assumption for the depth scale of these microcosm studies.

Solution of Equation IV-1 requires that the concentration gradient at the interface is known at a particular point in time; consequently, application of Equation IV-1 to the experimental results is extremely difficult. A more tractable approach is to fit an empirical model to the data which may then be differentiated to describe the instantaneous change in concentration as a function of initial concentration. In all cases, release over the duration of the experiment (9 days) can be described by the following logarithmic expression:

$$C_t = a + b \ln t \quad (\text{IV-2})$$

where C_t = the uniform concentration (mg/L) in the overlying water at time t (days), and

a (mg/L) and b (mg/L/d) are both empirically derived constants.

The rate of change in concentration is simply

$$\frac{dC}{dt} = b \cdot \frac{1}{t} \quad (IV-3)$$

Agreement of the data with the model, expressed in terms of the correlation coefficient, r , is presented in Table IV-2. Results from Aquaria 4 and 5 were combined because of the virtually identical water contents. Equation (IV-3) can be applied to evaluate the instantaneous change in concentration, and through mass balance considerations, the instantaneous areal release rate for a specified time. Average and instantaneous fluxes evaluated at the conclusion of the experiment are presented in Table IV-3.

Release rates averaged over the 9-day exchange period ranged from 1.57 to 22.7 mg P/m²-d and were inversely related to water content. These results were somewhat surprising and did not conform to a priori expectations; that is, if the concentration gradient is independent of the degree of dessication, sediments with greater water contents should yield higher diffusive fluxes because of the decreased tortuosity (Manheim 1970; Lerman 1979). Enhanced rates of detrital mineralization with increasing dessication and a concomitant elevation of interstitial SRP levels can account for the observed changes in flux; however, analyses conducted by Fox et al. (1977) of interstitial water SRP content in fresh and dried Lake Apopka sediments demonstrated essentially no difference between the two sediment types and thus do not substantiate this mechanism. A more likely mechanism is given by considering the change in sediment mass exposed on an areal basis as dessication proceeds. As pore water evaporates and the sediments

Table IV-2. Summary of Empirical Time-Dependent Concentration Model Parameters (Equation IV-2) and Goodness of Fit.

Aquarium	Water Content (percent)	a	b	r ²
1	88.30	0.0268	0.0417	.995
2	86.18	0.0231	0.0415	.992
3	34.31	0.0416	0.1137	.986
4 and 5	13.85	0.0032	0.1951	.919

Table IV-3. Calculated Average and Instantaneous Phosphorus Flux at Time = 9 Days During Passive Exchange Studies.

Aquarium	Average Flux (mg P/m ² -d)	Instantaneous Flux (mg P/m ² -d)
1	1.57	0.55
2	2.18	0.77
3	13.9	5.12
4 and 5	22.7	9.71

consolidate, increasing quantities of underlying sediment particles become directly exposed at the surface. A change in water content from 88 to 13 percent increases the exposed mass by approximately a factor of 10, which is close to the observed differences between the average flux from sediments 4 and 5 and from 1 and 2.

Additional experiments to quantify the passive exchange of P between Lake Apopka sediment and water were conducted using homogenized sediment from Station A5. Sediment was transferred to a series of three cylinders in sufficient quantity to yield a final depth of 14.5 cm. The diameter of the cylinders was 10.2 cm, resulting in a surface area of 81.7 cm^2 for exchange. The experiment was also designed to quantitatively evaluate the effects of dessication induced by lake drawdown on exchange; consequently two of the cylinders, B and C, were partially dessicated by insolation to yield final water contents of 91.66 and 89.14 percent, respectively. The final cylinder, A, was allowed to incubate at room temperature (22°C) for the duration of the dessication period (1 week). The water content of Cylinder A sediments was 94.89 percent. Following the dessication period, water was added to all three cylinders simultaneously. One liter of filtered, aged lake water from Lake Apopka, with an SRP concentration of 0.004 mg P/L, was added to each cylinder to serve as the solution phase; this maximized the concentration gradient across the sediment water interface and also removed any algae present.

During the incubation period the sediments in Cylinder A began to compact, lowering the sediment-water interface by approximately 0.7 cm and forming a residual interfacial pool of SRP enriched water. Subsequent extraction, filtration and analysis of 10 ml of the

interfacial water indicated an average concentration of 1.35 mg P/L. The interfacial water comprised a labile pool of approximately 64 ug P for immediate exchange upon addition of filtered lake water. Care was taken not to disturb the interface when the filtered lake water was added to each cylinder. Since the photic zone rarely extends below a depth of 0.9 m in Lake Apopka, the diffusional phase of the experiment was conducted in the dark. Free exchange with the atmosphere was permitted, however, to prevent the system from going anaerobic.

Changes in SRP concentration with time are shown in Figure IV-2 for all three cylinders. Cylinder A, representing fresh sediment, began the initial phase of the experiment with the highest concentration of SRP (0.192 mg P/L). Approximately 32 percent of this pulsed release was engendered by mixing of the residual interfacial pool with added lake water; the remaining release may have been induced by a slight disturbance of mud-water interface and subsequent entrainment of interstitial P and/or desorption from sediment particles. Because of this pulsed release, the concentration gradient was reduced and Cylinder A, consequently, showed the lowest rate of release. Calculations of release rates were based upon observed changes in SRP in the overlying water during the initial phase of the experiment, when the concentration gradient was most extreme and the resulting overlying water concentrations approximated ambient SRP levels observed in situ. Release rates were essentially linear during this phase, and as seen in the previous exchange studies with A2 sediment, release increased as an inverse function of sediment water content. Release from Cylinder A approximated $4.3 \text{ mg P/m}^2\text{-d}$ while release from Cylinder C was calculated to be $28.8 \text{ mg P/m}^2\text{-d}$, (Table IV-4). Observed rates of

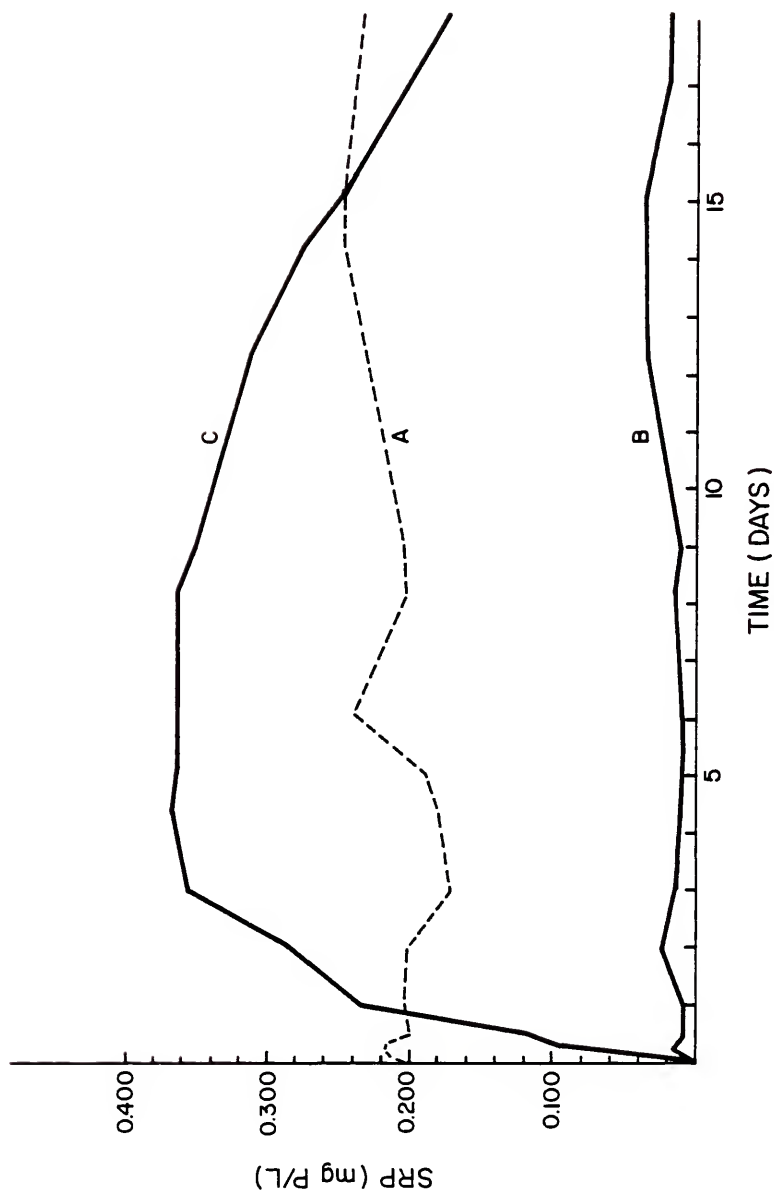


Figure IV-2. Passive (Diffusive) Release of SRP by Fresh (A) and Partially Dessicated (B and C) Lake Apopka Sediments (Station A5) with Time. See Text for Water Content Concentrations.

Table IV-4. Calculated Porosities, Diffusive Fluxes, and Tortuosity Corrected Molecular Diffusivities for Fresh and Partially Dessicated Lake Apopka Sediment.

Cylinder	Water Content (percent)	Porosity (Dimensionless)	Corrected Molecular Diffusivity D ($\text{cm}^2/\text{s} \times 10^6$)*	Diffusive Flux Observed ($\text{mg P}/\text{m}^2\text{-d}$)
A	94.89	0.9716	6.93	4.3
B	91.66	0.9551	6.70	6.9
C	89.14	0.9408	6.50	28.8

* Using a D_0 value of $7.34 \times 10^{-6} \text{ cm}^2/\text{s}$ for HPO_4^{-2} at 25°C (Li and Gregory 1974).

release for Cylinders A and B are comparable to other values reported in the laboratory for undisturbed cores (Table IV-5). In addition to the previously described hypothesis regarding sediment exposure and dessication, the observed flux in Cylinder A is also undoubtedly lower because of the reduced concentration gradient across the sediment-water interface. This effect can be derived directly from Fick's first law of diffusion where flux is proportional to the concentration gradient. This effect has also been empirically verified by Rippey (1977) who observed that maintenance of low concentrations in the overlying water of undisturbed cores increased areal release rates by 82 percent.

For Cylinders A and B, the linear phase of rapid release was confined to an extremely short timeframe of 6 hours beyond which decreases in concentration approaching initial levels occurred. Concentrations in Cylinder A remained relatively stable for the next 42 hours, but by 72 hours they showed a further decline to a minimum concentration of 0.172 mg P/L. After 72 hours, release was again essentially linear in Cylinder A, and approximated $0.6 \text{ mg P/m}^2\text{-d}$. Similar erratic behavior was observed in Cylinder B; between 6 hours and 48 hours SRP levels fell to 0.007 mg P/L and then proceeded to increase towards a secondary maximum of 0.023 mg P/L at 48 hours. Between 121 and 362 hours, SRP concentrations steadily increased. Release during this period equalled $0.3 \text{ mg P/m}^2\text{-d}$. Although the concentration gradient was more pronounced in Cylinder B, the reduced flux after the initial equilibration stage is more consistent with the decline in overall porosity and the formation of a relatively impermeable crust caused by partial dessication.

Table IV-5. Summary of Reported Sediment Phosphorus Release Rates Measured In Situ and in the Laboratory.

Lake	Experimental System	Temperature (°C)	Release Rate (mg P/m ² -d)		Reference
			Aerobic	Anaerobic	
Norvikken	Laboratory-core	4	1.7 - 3.0	3.0 - 4.6	Ulen (1978)
	Laboratory-core Calculated (diffusion)	10 --	2.4 - 6.7 1.0	4.0 - 7.3	
Esrom	Undisturbed cores		-8 - 16.2		Kamp-Nielsen (1975)
Esrom	Undisturbed core	7	-1.4	12.3	Kamp-Nielsen (1974)
Gnadensee		4 10 15 25	1.2 2.2 3.5 9.4		Banoub (1975)
Sodra Bergundas-Jon	Undisturbed core	8		36	Bengtsson (1975)
Lough Neagh	Undisturbed core	10	10.4		Rippey (1977)
	Agitated core		14.8		
Lough Neagh	Calculated		14 - 48		Stevens and Gibson (1977)
Warner	In situ-calculated		26		Digiano and Snow (1977)
Castle	In situ		0.65		Neame (1977)
Mohegan	Homogenized	20	-2.5	2 - 3	Fillos and Biswas (1976)
Mendota	Undisturbed	2-23	-1.9 - 83	0.67 - 65	Holdren and Armstrong (1980)
Wingra	Undisturbed	4-21	-0.56 - 3.4	0.95 - 2.9	Holdren and Armstrong (1980)
Minocqua	Undisturbed	3-18	<0.02 - 0.37	0.03 - 3.1	Holdren and Armstrong (1980)
Little John	Undisturbed	4-16	<0.02 - 1.1	0.02 - 3.8	Holdren and Armstrong (1980)
Shagawa	In situ			7	Sonzogni et al. (1977)

Fox et al. (1977) conducted similar experiments with Lake Apopka sediments to determine the effects of dessication on overlying water quality. A general pattern of increasing P release with extent of dessication was observed. Release as a function of dessication for both this study and that of Fox et al. (1977) is presented in Figure IV-3 for equilibration times of 144.5 hours and 1 week, respectively. Linear regression analysis indicates a highly significant relationship between the two variables ($r^2 = .74$, $p < 0.025$), yielding the following model:

$$SL = 1.44 - 0.01 W \quad (IV-4)$$

where SL = concentration (mg P/L) observed after the stated equilibration times, and
W = percent water content of the sediment.

The most consistent behavior with respect to release was observed for the most dessicated sediment, Cylinder C. Release was relatively constant over the initial 24 hours and began to decrease, apparently in response to the diminished concentration gradient. Net release continued until a state of dynamic equilibrium was achieved by Day 4, when uptake essentially balanced release. Equilibrium was maintained for approximately the next 93 hours following which time concentrations dropped steadily for the duration of the experiment. The subsequent decline in SRP is probably biological in nature; the longer period of exposure to insolation and incident UV radiation undoubtedly had a pronounced, deleterious effect on the benthic microflora in Cylinder C relative to the other cylinders. If benthic microbial activity

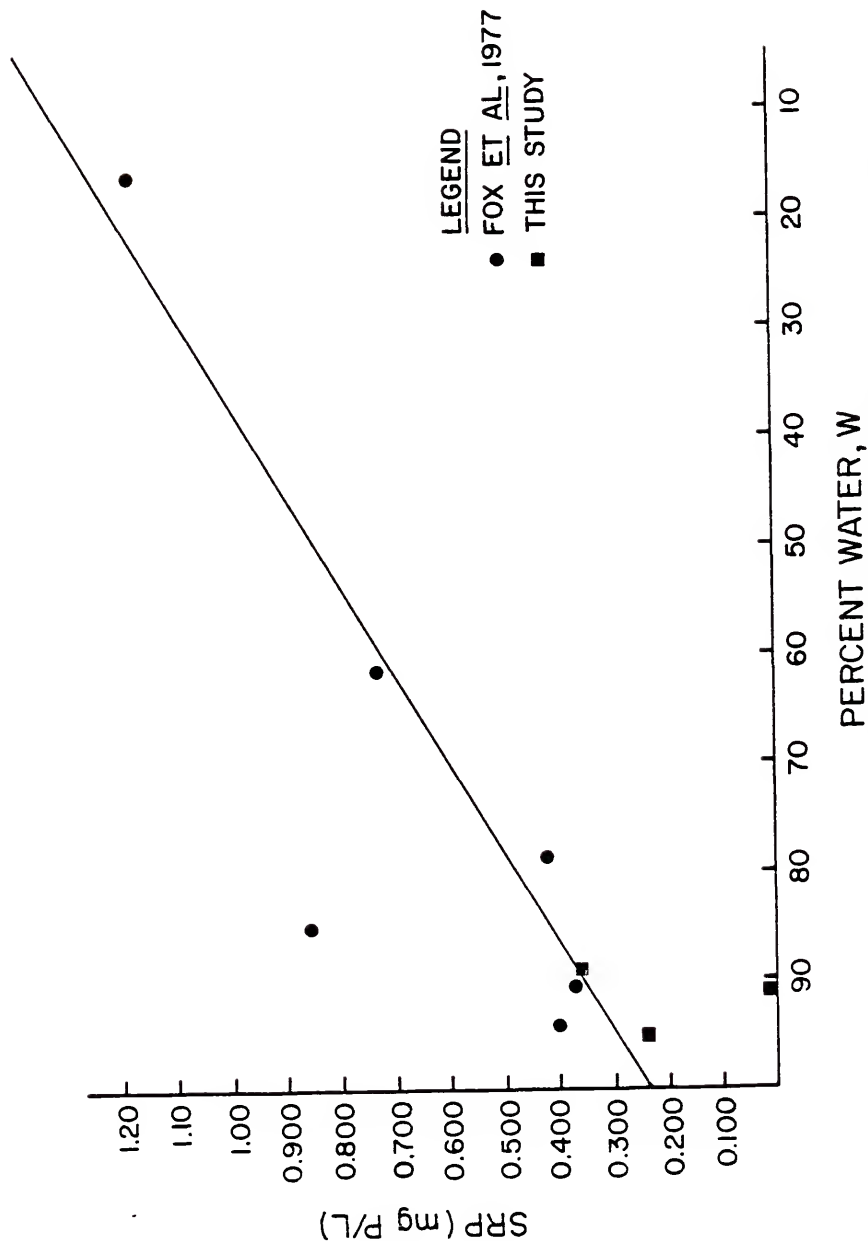


Figure IV-3. Equilibrium SRP Levels in Laboratory Aquaria (Fox et al. 1977) and Cylinders (this study) as a Function of Sediment Dessication. Concentrations Represent Equilibration Times of 168 Hours and 144.5 Hours, Respectively.

increased as the experiment progressed a concomitant increase in SRP uptake should have been observed; this mechanism is consistent with the observed decline in SRP. It is interesting to note that concentrations of SRP in both Cylinder A and B remained relatively constant during the latter stages of the experiment; this may indicate that the benthic microbial community was stable from the outset.

Calcium and magnesium concentrations were monitored during the course of the study. Magnesium levels were essentially constant when corrected for evaporative effects whereas corrected calcium levels show a substantial increase of approximately 14 mg/L by the end of the experiment. Sedimentary CaCO_3 is apparently solubilized as a result of heterotrophic activity producing CO_2 (Lee et al. 1977). The magnitude of Ca release for all three cylinders was approximately the same, and thus solubilization of hydroxyapatite was not the primary mechanism for release since the amount of P release differed markedly among the cylinders.

Turbulence Study

As an extension of the quiescent nutrient release study conducted with sediments from Station A5 in Lake Apopka, the effects of turbulence on SRP exchange also were evaluated. After equilibration periods of 35 to 45 days to dampen phosphorus concentration changes associated with diffusion, Cylinders A and C (representing fresh and partially dessicated sediments, respectively) were subjected to varying degrees of turbulence with a variable speed rotor with a paddle attachment. The paddle encompassed a surface area of 21 cm^2 and was situated 4.4 cm

above the sediment-water interface. The depth of the water column for each system was maintained at approximately 11.2 cm.

Samples for SRP were withdrawn immediately preceding the start of each experiment; subsequent samples were taken at measured time intervals. All samples were filtered through GF/C glass microfibre filter paper. Supplemental aliquots also were removed at periodic intervals to determine suspended sediment concentrations. Equivalent quantities of aged and filtered water from Lake Apopka were introduced into each cylinder after each sample was withdrawn in order to maintain a constant volume.

Fresh Sediment

Results of the turbulence experiment with fresh Lake Apopka sediment are depicted in Figures IV-4 and IV-5. The initial phase was conducted at a stirring velocity of 10.5 to 12.2 revolutions per minute (rpm) sustained for 62 minutes. This velocity was sufficient to entrain isolated, loose sediment particles at the interface, although the interface remained essentially intact. Upon lowering the velocity to 9.0 rpm, the suspended particles began to settle. A net decline (corrected for sample removal) of 0.002 mg P/L was observed during this period, indicating virtually no effect of stirring at this rate on equilibrated sediment.

The system was allowed to remain quiescent for another 67 minutes before initiation of a second turbulence period. Rotor velocity was increased to a maximum of 67.6 rpm, causing immediate scour of the interface. Turbulence was maintained for exactly 1 hour. After a

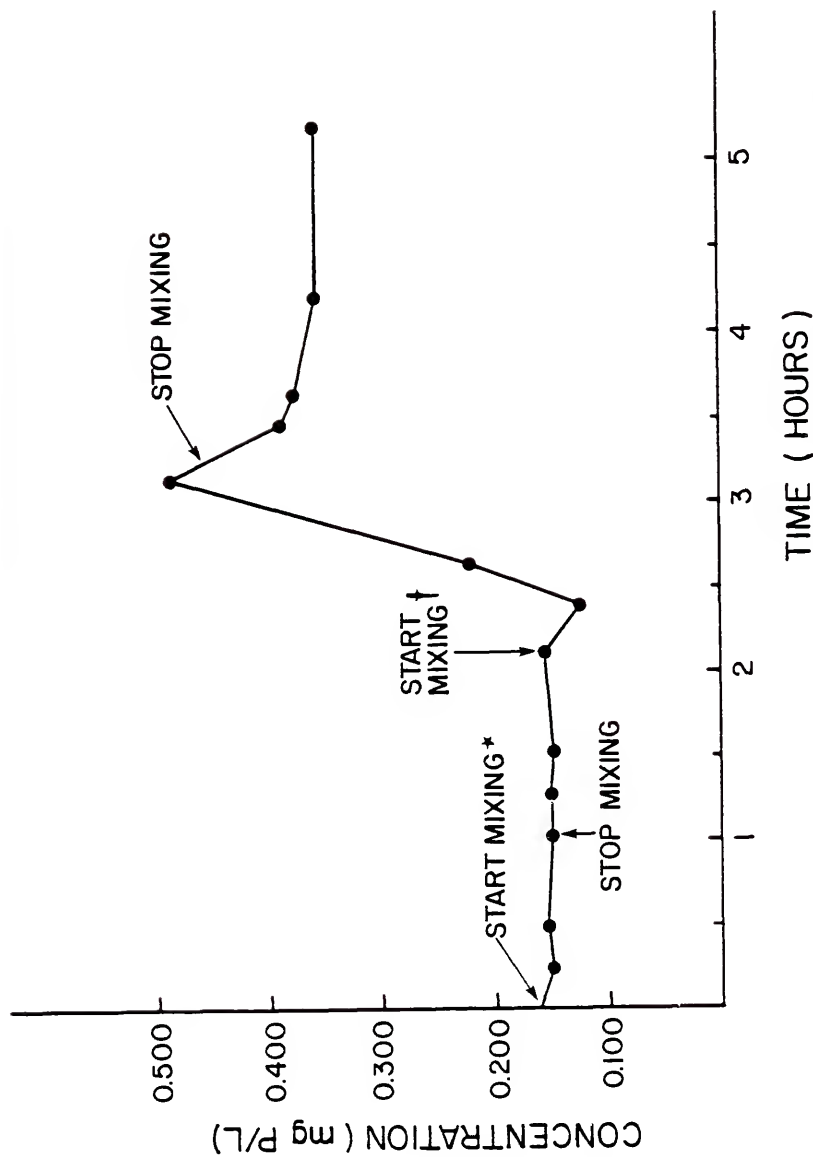


Figure IV-4. Effect of Turbulence on SRP Concentrations in Water Overlying Fresh Lake Apopka Sediments.

* Sediment not resuspended.

† Sediment resuspended.

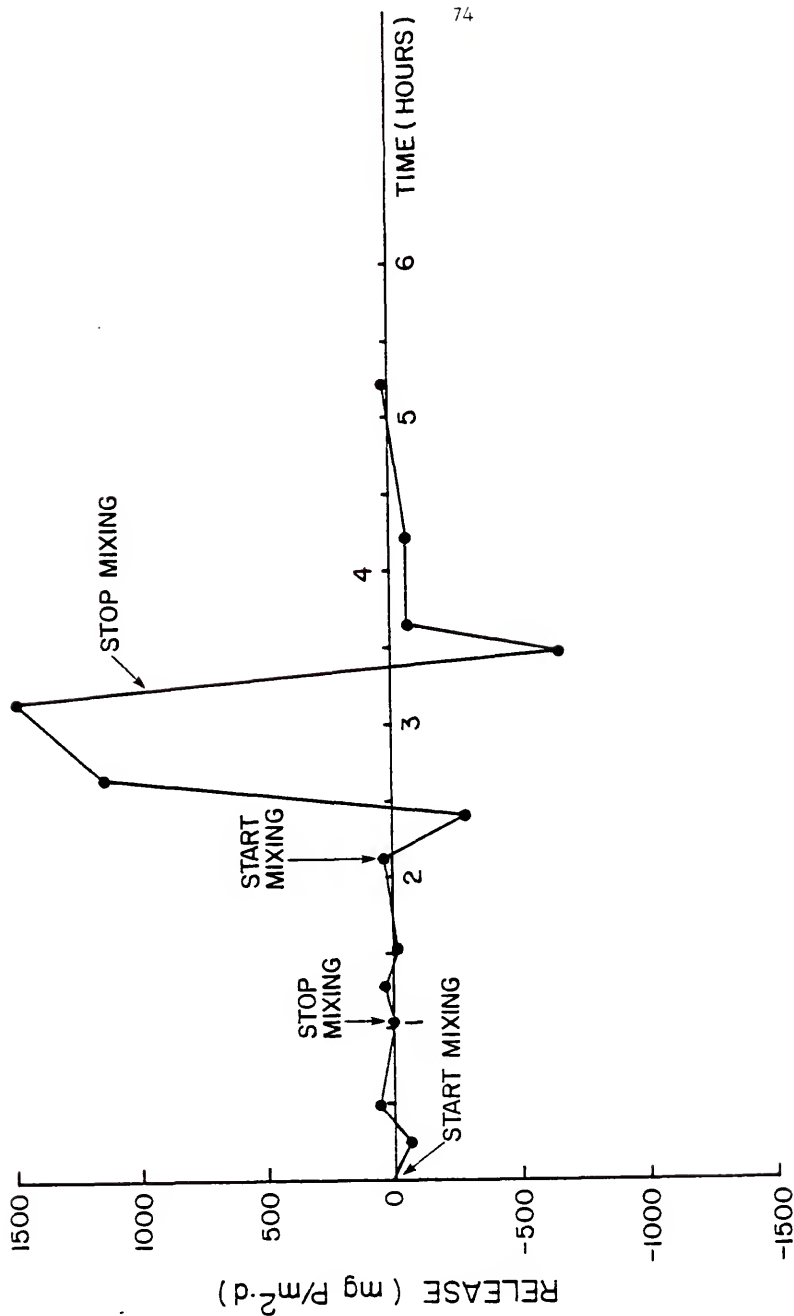


Figure IV-5. Effect of Turbulence on SRP Release Rates from Fresh Lake Apopka Sediments (Station A5).

preliminary reduction in concentration of SRP in the overlying water at the start of turbulence, SRP levels increased to 0.484 mg P/L and suspended sediment concentrations reached 12.61 g/L by the conclusion of the turbulent phase. Mass balance calculations indicate that between 25 to 68 percent of the net release in SRP was the result of entrained interstitial water; the remaining fraction was apparently desorbed from suspended particles and was equivalent to desorption of 12.3 to 28.4 ug P/g. More exhaustive studies concerning sorption phenomena are presented elsewhere (see Section V, Adsorption-Desorption Studies). The contribution of the pore water to release was calculated by assuming that the concentration of SRP was between 0.50 to 1.35 mg P/L; the latter value represents the interfacial water concentration at the beginning of the diffusion study following exposure whereas the former value constitutes the interstitial water content of the fresh sediment prior to exposure. If release during the quiescent study is assumed to be strictly diffusive, then 33 percent of the observed net release can be attributed to entrainment of the pore fluid and the magnitude of desorption approximates 25.6 ug P/g.

After stirring was concluded, resuspended sediment particles began to settle rapidly, establishing a sharp interface between a clear supernatant and the settling particles. Migration of the interface was relatively slow (2.57×10^{-3} cm/s) during the first 7 minutes after cessation of stirring because of turbulence within the water column (Figure IV-6). After this equilibration period, water motion within the cylinder became dampened and the settling velocity was much more rapid. As the interface approached the point of origin, velocities decreased in

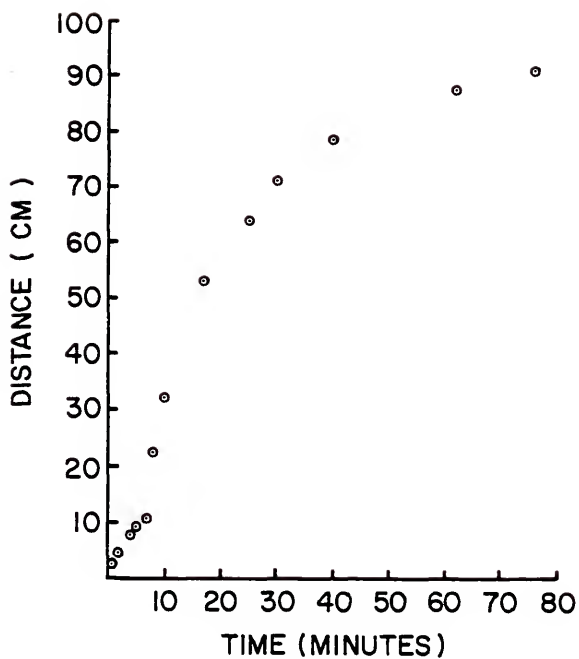


Figure IV-6. Migration of Interface Between Suspended Sediment and Clear Supernatant with Time Following Cessation of Turbulence.

response to resistance from the compacted particles. The maximum observed settling velocity was 1.95×10^{-2} cm/s. Some readsorption of phosphorus occurred as the entrained sediment particles settled; however, a significant increase in concentration relative to initial SRP levels was observed after equilibrium had been established. The final concentration was 0.355 mg P/L compared with an initial concentration of 0.159 mg P/L. These results conflict with Holdren and Armstrong (1980) who observed that P release from Lake Mendota sediments generally increased with increased stirring up to the point where sediment suspension occurred. Resuspension was found by Holdren and Armstrong (1980) to decrease overlying water SRP concentrations to levels below those in unstirred cores. Conversely, resuspension of Lake Apopka sediments results in a substantial release of SRP, while stirring in the absence of resuspension has virtually no effect on release. Indeed, in the experimental system employed in this study, no change in SRP levels was anticipated with stirring up to the point of bed failure because the system was allowed to equilibrate for an extended timeframe. In other words, the initial conditions of the experiment set $\partial c / \partial t = 0$, which according to Fick's second law implies that any change in the diffusivity constant caused by stirring will not alter the concentration of SRP in the overlying water. In the cores used by Holdren and Armstrong (1980), the derivative of the concentration gradient is non-zero; thus, an increase in diffusivity induced by stirring will result in a concomitant increase in $\partial c / \partial t$.

Partially Dessicated Sediment

The effect of turbulence on SRP release from partially dessicated sediments (Cylinder C) was minimal. As in the preceding experiment on Cylinder A, the sediments of Cylinder C were subjected to two discrete periods of turbulence separated by a quiescent phase to isolate any observed effects. The initial turbulent phase was conducted at an average rotor velocity of 13.9 rpm maintained for 1 hour. Concentration changes were somewhat erratic during this phase (Figure IV-7) and when corrected for sample removal and replacement with filtered Lake Apopka water were equivalent to a net release of only 0.001 mg P/L. Rotor velocity was insufficient to disturb the sediment-water interface, although some unconsolidated particles were entrained.

After a stabilization period of nearly 2 hours during which the overlying water SRP concentration remained essentially constant, turbulence was again induced. Rotor velocity was increased to 115.5 rpm and was allowed to continue for exactly 2 hours. Despite the extreme amount of turbulence, the interface remained intact except for some erosion from a small hole initially created by the removal of a sediment subsample for analysis. A steady-state suspended sediment concentration of only 0.0720 g/L was observed after 90 minutes. No phosphorus desorption was detected in association with the minor amount of sediment resuspended; however, a small but discernible decrease in concentration of SRP in the overlying water did occur. The net decrease when corrected for sample removal was 0.004 mg P/L and corresponds qualitatively to the initial decrease observed in Cylinder A when resuspension was induced. The apparent mechanism for the loss from solution is

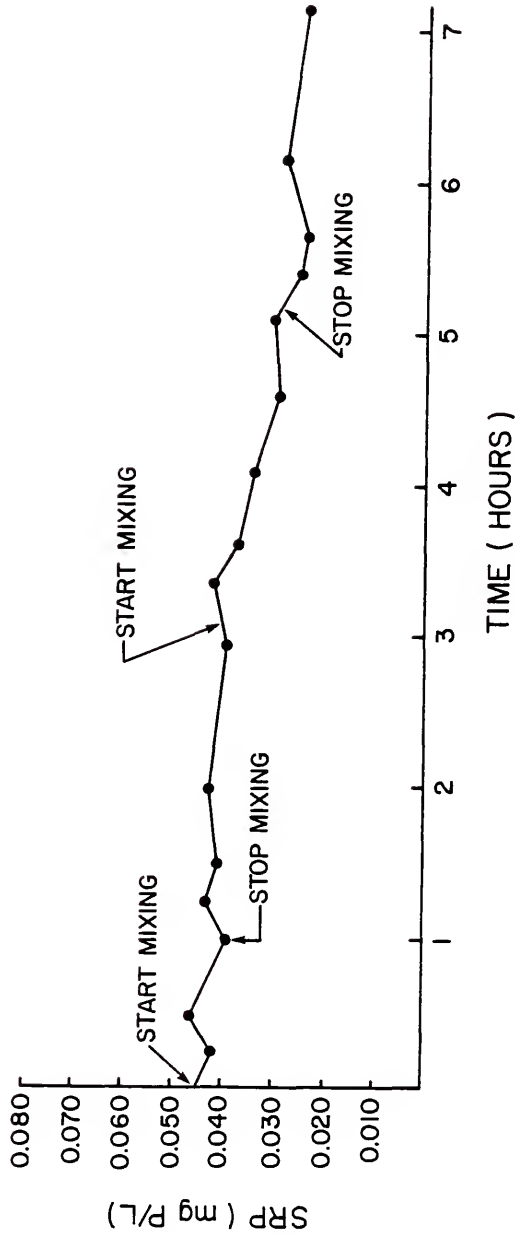


Figure IV-7. Effect of Turbulence on SRP Concentrations in Water Overlying Partially Dessicated (Cylinder C) Lake Apopka Sediments.

adsorption by resuspended particles derived from the surface; due to a period of desorption and diffusive loss during the month long quiescent equilibration phase, the surface particles apparently have less surface-sorbed P than underlying sediments. Because of the reduction in surface coverage of available binding sites (see Section V, Sorption Characteristics), the relatively impoverished surface particles are free to adsorb P upon resuspension. Further scour of underlying sediments entrains surface-P rich particles which then undergo desorption (e.g., Cylinder A). The extent of scour in Cylinder C was apparently not sufficient to resuspend these enriched particles; thus, a net decline in SRP was observed.

The results of this experiment indicate that even partially dessicated sediments are very stable and will not be resuspended even under conditions of extreme turbulence. However, if the oxidized surface layer is breached, exposing the less compacted sediments lying underneath, localized scour is likely to occur.

In-Situ Studies

Water quality and limnological monitoring of Lake Apopka was conducted between January 1977 and January 1981 as an integral part of the Lake Apopka restoration program. The results of the study have been presented elsewhere for individual years (Brezonik et al. 1978; Tuschall et al. 1979; Pollman et al. 1980; and Brezonik et al. 1981) and will not be discussed here except to relate observed chemical characteristics with the phenomenon of internal loading. Monitoring within Lake Apopka focused on three open-water stations (A2, A5, and A8) and Gourd Neck

Springs for the bulk of the study after a comprehensive survey of 11 stations during the first year showed that adequate spatial characterization was provided by three sampling points. Sampling was conducted monthly except for the first year when the frequency was biweekly.

To evaluate the degree of interaction between SRP concentrations and other chemical components, a correlation matrix was developed using SAS (Statistical Analysis System) (Barr et al. 1976). Correlation analysis compares parameters by way of a linear model to determine if a significant relationship exists. The degree of linear correlation between the two variables is given by the correlation coefficient, r , which by definition must lie between 1 and -1. Selected results of the analysis are presented in Table IV-6. Using the 5 percent confidence level as the threshold of significance, significant relationships between SRP and other abiotic variables were established for only two parameters: turbidity and inorganic carbon (IC). Although a simple correlation between two variables is not conclusive evidence of a cause and effect relationship, this result does suggest that SRP levels within Lake Apopka are influenced by the resuspension of sediments.

Indirect evidence to substantiate the role of sediment resuspension of phosphorus dynamics is offered by evaluating the interaction between turbidity and ammonia variability. Correlation analysis (Table IV-6) indicates these two parameters are significantly related. Ammonia, which is generated by heterotrophic bacteria as organic matter is

Table IV-6. Intercomponent Relationships Between Selected Variables in Lake Apopka, 1977 to 1980.

	Turbidity	IC	K	Ammonia	Color
SRP	0.28915 (0.0487)	0.38099 (0.0082)	0.30150 (0.0621)	0.12823 (0.3904)	-0.14958 (0.3156)
Turbidity		0.65573 (0.0001)	0.72893 (0.0001)	0.32722 (0.0248)	0.01153 (0.9387)
IC			0.90591 (0.0001)	0.10961 (0.4633)	-0.20465 (0.1676)
K				-0.00954 (0.9541)	-0.10756 (0.5145)
Ammonia					-0.03957 (0.7917)

Note: () = significance of relationship.

decomposed, accretes in sedimentary pore fluids to quite significant levels. Concentrations as high as 49.0 mg N/L have been observed in Lake Apopka sediments (Brezonik et al. 1978). Average interstitial concentrations exceed typical levels in the overlying water of Lake Apopka by over two orders of magnitude; thus even minor disturbances of the sediment-water interface can exert a profound influence on the nutrient status of the water column. Seasonal dynamics of nitrogen in Lake Apopka are stochastic in nature, apparently as a result of episodic disturbances and scouring of the bottom sediments.

SRP was strongly correlated ($p = 0.0082$) with inorganic carbon and to a lesser extent ($p = 0.0621$) with potassium. Similar to ammonia, inorganic carbon accumulates in the interstitial fluid as detrital material is metabolized. Likewise, the close relationship between turbidity and inorganic carbon ($r = .656$, $p = 0.0001$) (Table IV-6) supports a resuspension type of mechanism for controlling to a significant extent the concentration of this solute in the overlying water. Potassium, which in turn is very closely related to inorganic carbon ($r = .729$, $p = 0.0001$), is essential for aerobic life forms (Lehninger 1970) and has been used as a tracer for the migration through soils of leachate derived from decomposing vegetative material (Ellis 1980). Wetzel (1975) has observed that potassium levels can be depleted in the trophogenic zone of highly productive lakes presumably due to biotic uptake and in turn accumulate in the tropholytic zone. It consequently seems reasonable to label K as an indicator of internal nutrient cycling and, in particular, nutrient release induced by sediment resuspension.

If the internal dynamics of phosphorus cycling in Lake Apopka are dominated by external loading, a simple correlation between external loading (or a corollary parameter) and SRP can be anticipated. A nutrient budget developed for the 1977 water year has identified maintenance backpumping of the muck farms bordering the northern perimeter of Lake Apopka as the principal external source of phosphorus. Because of the high organic content of the muck soils, the nutrient-enriched soil water is highly colored. This characteristic provides a convenient marker with which to trace the discharge of agricultural wastes and associated nutrients to the system. The following example illustrates this point. During late summer 1979, the Apopka drainage basin experienced heavy rainfall and high rates of backpumping to the lake and the Apopka-Beauclair canal were observed. The effect of agricultural discharge on Lake Apopka and the downstream Oklawaha lakes was striking, as illustrated in Figure IV-8 which delineates the spatial distribution of both color and SRP during September 1979. Concentrations in both SRP and color show an increase with location moving towards the north end of the lake. Once within the Apopka-Beauclair canal, SRP and color concentrations increased dramatically. Color and SRP concentrations at the outfall of a discharge pipe on the Apopka-Beauclair canal were 101 chloroplatinate units (CPU) and 0.523 mg P/L, respectively; this is contrasted with substantially lower color (65 CPU) and SRP (0.026 mg P/L) concentrations at the outlet of the lake. Figure IV-8 shows that SRP concentrations and color appear to be intrinsically linked; both parameters decrease monotonically with distance downstream from the source until the Dora canal is reached. Similar observations were made during August and October 1979.

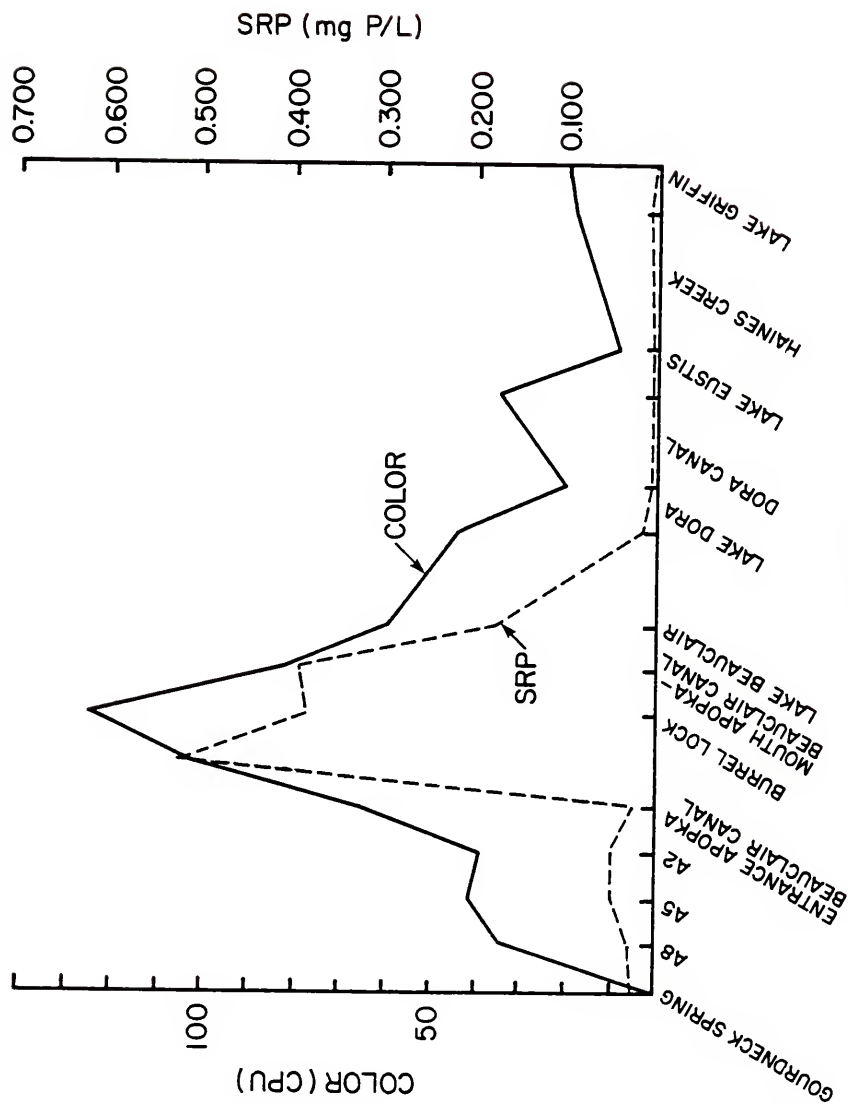


Figure IV-8. Variations in SRP (mg P/L) and Color (CPU) with Distance along the Oklawaha Chain of Lakes, September 28, 1979. From Pollman et al. (1980).

If color is a reasonable label to trace long-term influences of external loading on SRP dynamics, correlation analysis for the 4-year data base implies that the relationship is insignificant. A weak, negative correlation ($r = -.14958$, $p = 0.3156$) was derived between color and SRP, suggesting that SRP variability within Lake Apopka is independent of external inputs.

On July 11, 1979, a brief but intense convective disturbance was encountered on Lake Apopka at the beginning of a routine sampling effort. The storm, which originated from the southwest, began at approximately 1540 hours. Wind velocities were estimated to range between 9 and 11 m/s at the advent of the storm and had diminished to approximately 6.7 m/s by the time the last sample was taken 1 hour later. As the storm swept across the lake surface, bottom sediments were immediately resuspended to the surface. The visual change was rather remarkable; for example, sediment resuspension was observed as a sharp front normal to and moving across the lake in the same direction as the wind. Behind the front the water surface assumed a muddy brown appearance from entrained sediments while on the leeward side, a characteristic greenish cast typical of the highly productive water column was observed.

Turbidity and suspended solids measurements from a protected point along the western edge of the lake near Gourd Neck Springs showed concentrations of 31 NTU and 0.0865 g/L of suspended material at the surface. These values were considered to be representative of background or pre-storm conditions. Surface samples from the open-water stations (A2, A5, and A8) readily showed the effects of resuspension;

turbidities ranged from 43 to 46 NTU and suspended sediment concentrations ranged from 0.2053 to 0.2553 g/L.

Composite samples were taken from the surface and 1-m depth at the open-water points and analyzed for turbidity, SRP, and TP. Results are presented in Figure IV-9. Turbidity levels at all three stations were substantially higher in the composited samples relative to surface specific samples, thus indicating that resuspension was not uniform throughout the water column but existed in the form of a concentration gradient. Lakewide average turbidity and SRP concentrations both exceeded levels observed the previous month during quiescent conditions by a factor of three (Pollman et al. 1980). SRP levels were particularly high at Station A5 where a concentration 0.277 mg P/L was observed. Although the composited turbidity concentration was lower at this station (90 NTU) relative to Stations A2 and A8 (100 and 120 NTU, respectively), sampling was conducted at this station during the waning moments of the disturbance. Wind velocity and wave activity were much reduced at Station A5, allowing entrained particles to resettle. Kinetic factors may also account for the lower SRP concentrations observed at Stations A2 and A8.

Although suspended sediment concentrations are unavailable for the composited samples, an empirical relationship derived in situ between turbidity and suspended solids for Lake Apopka (Figure IV-10) enables an estimate of the quantity of sediment resuspended to be made. The following linear model was derived from least squares regression analysis ($r^2 = .96$, $p < 0.025$):

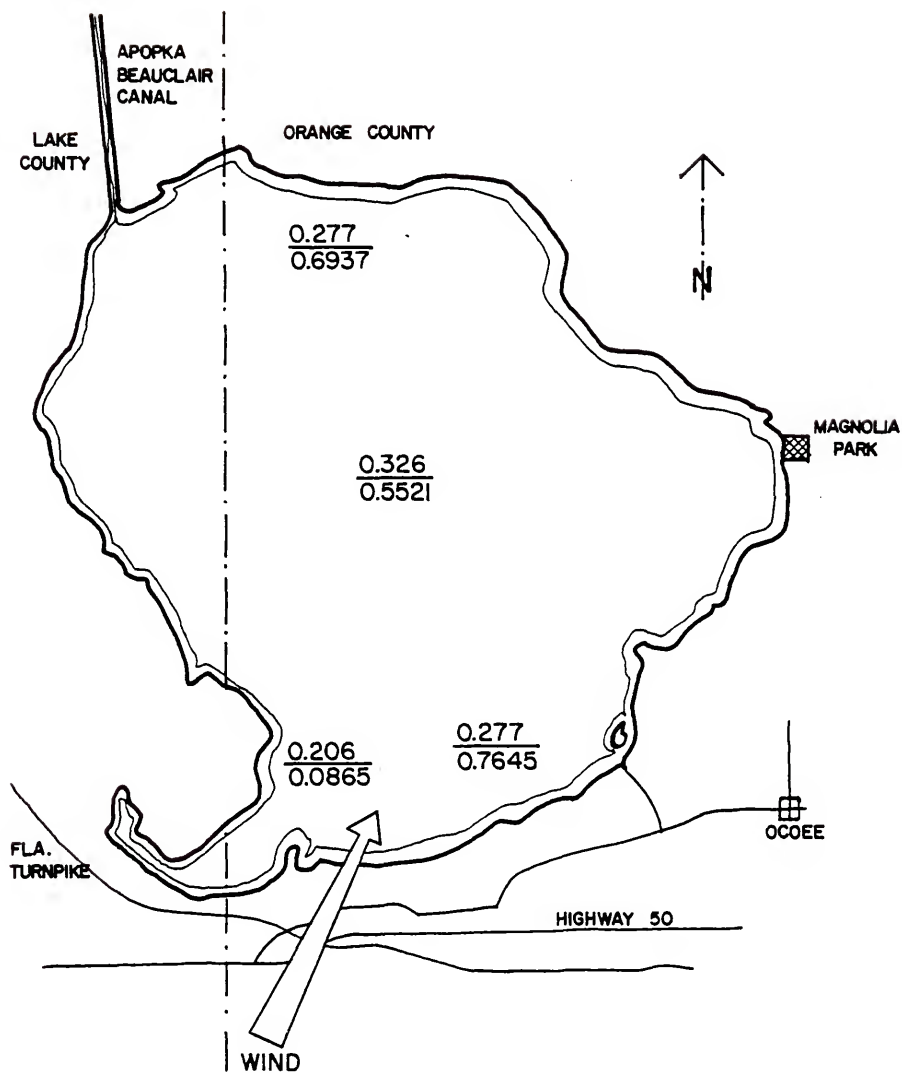


Figure IV-9. Suspended Sediment (g/L) and Total Phosphorus (TP) (mg P/L) Concentrations in Lake Apopka During a Convective Disturbance, July 11, 1979. TP and Suspended Sediment Concentrations are Presented as the Upper and Lower Figures, Respectively, at Each Sampling Site.

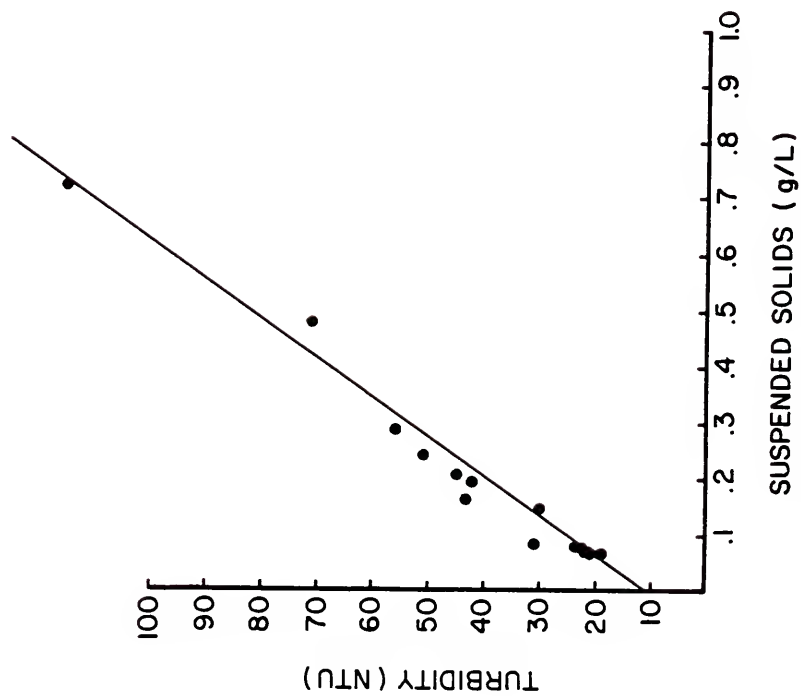


Figure IV-10. Turbidity (NTU) in Lake Apopka as a Function of Suspended Solids (g/L).

$$\text{Turbidity} = 12.04 + 141.2 (\text{SS}) \quad (\text{IV-5})$$

where SS is the concentration of suspended solids (g/L), and turbidity is given in NTU. On the basis of this model, the sediment concentration yielding the observed composite turbidity levels can be determined.

Using data from Station A5 as an example, a turbidity concentration of 90 NTU equates to a suspended solids concentration of 0.5521 g/L. The suspended sediment concentration at 1-m depth must therefore be equal to 0.8973 g/L. Assuming the concentration of suspended matter increases linearly with depth gives an average concentration for the water column ($z = 176$ cm) of 0.8145 g/L.

Correcting for the background contribution from ambient phytoplankton and suspended sediment concentrations (0.0696 g/L) yields a net resuspension of 0.7449 g/L. The areal loss across the sediment water interface is therefore $1,311 \text{ g/m}^2$. Since the average bulk density and water content of Lake Apopka sediments is 1.024 g/cm^3 and 96.04 percent, respectively, the depth of the sediment entrainment is estimated to be 3.2 cm. Calculated depths of sediment resuspension for Stations A2 and A8 are summarized in Table IV-7.

Table IV-7. Estimated Depth of Sediment Resuspension of Lake Apopka During a Convective Disturbance, July 11, 1979.

Station	Depth (cm)	Composite Turbidity (NTU)	Calculated Composite Suspended Sediment Concentration (g/L)	Surface Suspended Sediment Concentration (g/L)	Calculated Depth of Resuspension (cm)
A2	180	110	0.6937	0.1616	4.7
A5	176	90	0.5521	0.2069	3.2
A8	150	120	0.7645	0.2553	3.5

CHAPTER V NUTRIENT RELEASE MODEL

A series of adsorption-desorption isotherm studies were conducted in the laboratory to determine net release or uptake of phosphorus as a function of ambient levels of SRP in the water under well-mixed (equilibrium) conditions. Experimental results indicate that Lake Okeechobee sediments vary appreciably in their ability to adsorb (or desorb) phosphorus. A characteristic curvilinear relationship between initial concentration and the magnitude of sorption was observed for all stations except Station 013, which showed little ability to desorb or absorb phosphorus over the experimental range of concentrations (Figures V-1 through V-4). Similar curvilinear results were reported by Harter and Foster (1976) and Mayer and Gloss (1980). A station-by-station comparison of adsorption at an initial concentration of 1,000 ug/L suggests that Station 07 sediments have greatest affinity for phosphorus at high concentrations; these sediments also have the greatest silt-clay content, and thus the greatest surface area available for exchange. Because of their relative homogeneity with respect to chemical and physical characteristics, sorption studies with Lake Apopka sediments were limited to sediment from Station A5. A curvilinear relationship between the extent of sorption and initial concentration was also observed for Station A5 sediment; the results, however,

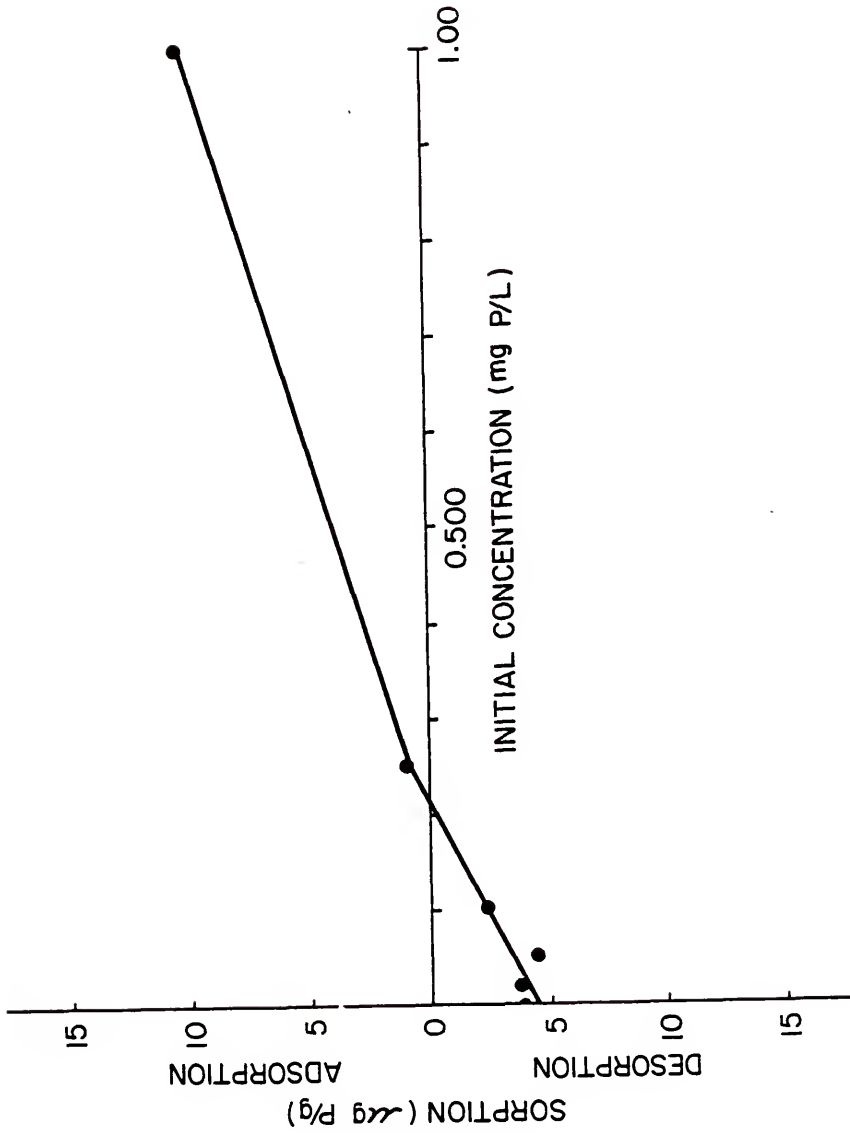


Figure V-1. SRP Sorption by Station 010 Sediments as a Function of Initial SRP Concentration.

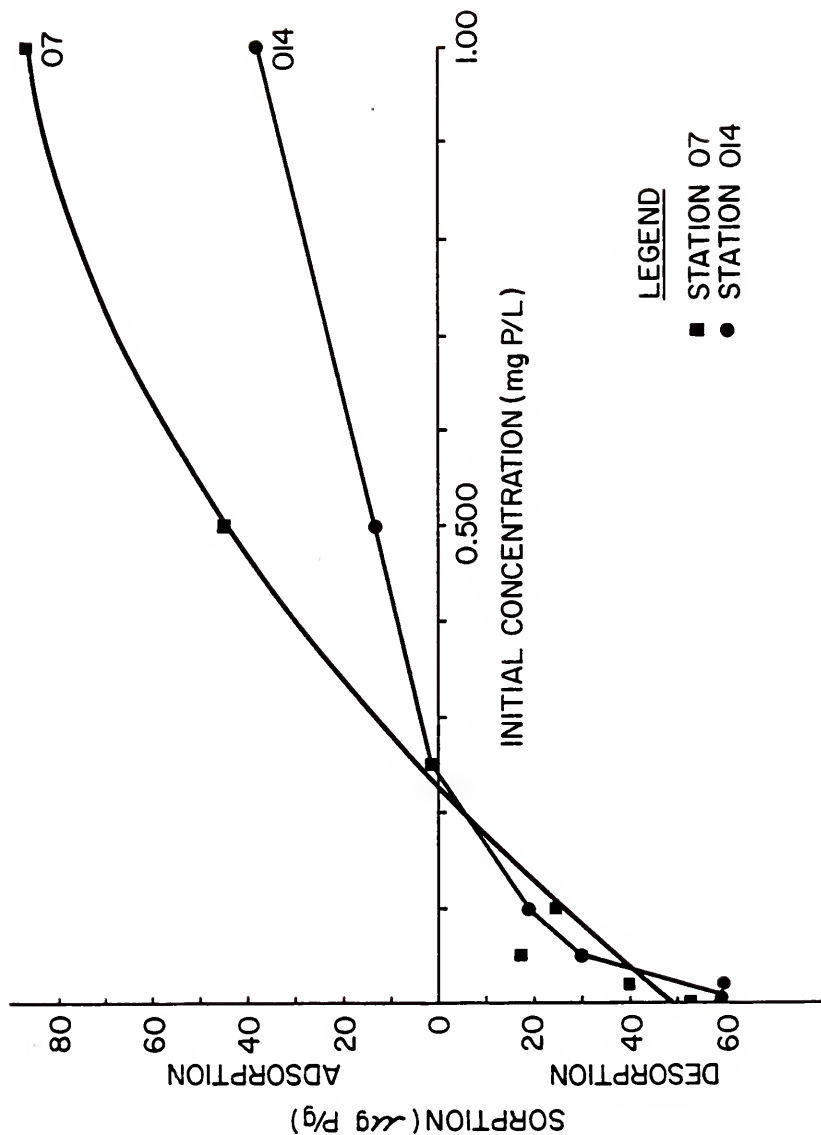


Figure V-2. SRP Sorption by Station 07 and Station 014 Sediments as a Function of Initial SRP Concentration.

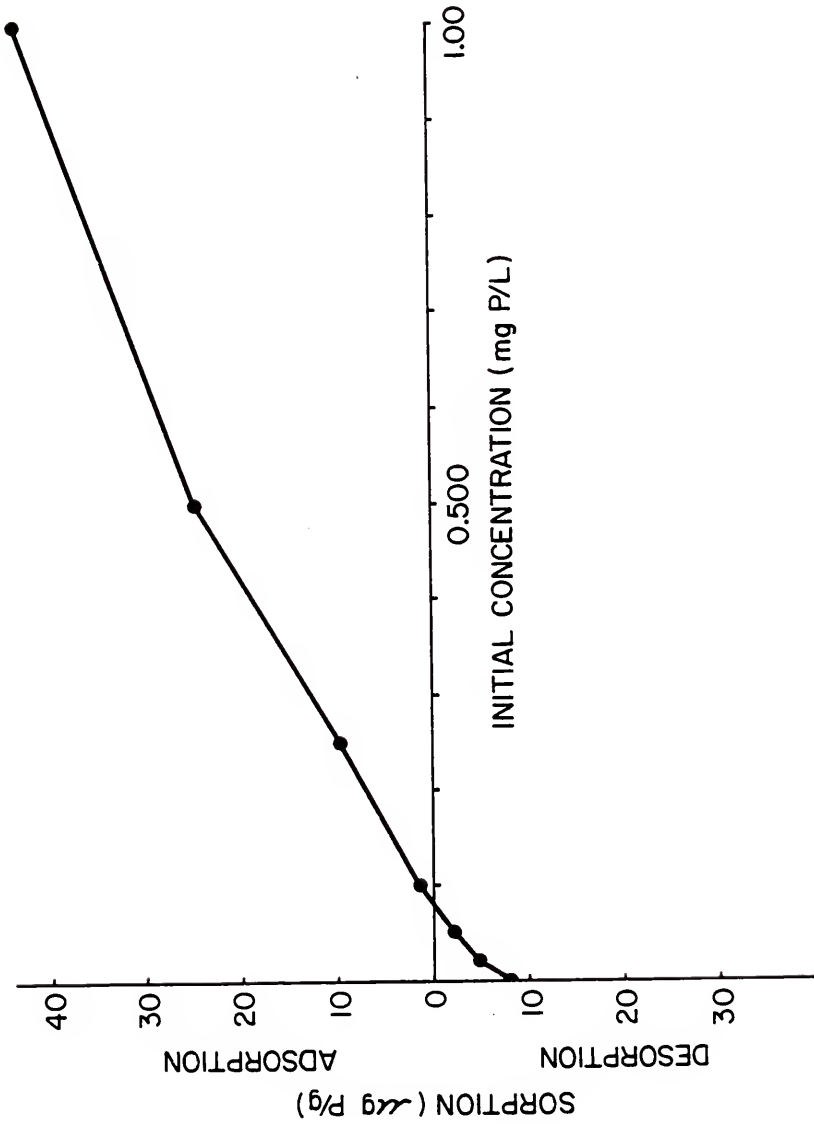


Figure V-3. SRP Sorption by Station 011 Sediments as a Function of Initial SRP Concentration.

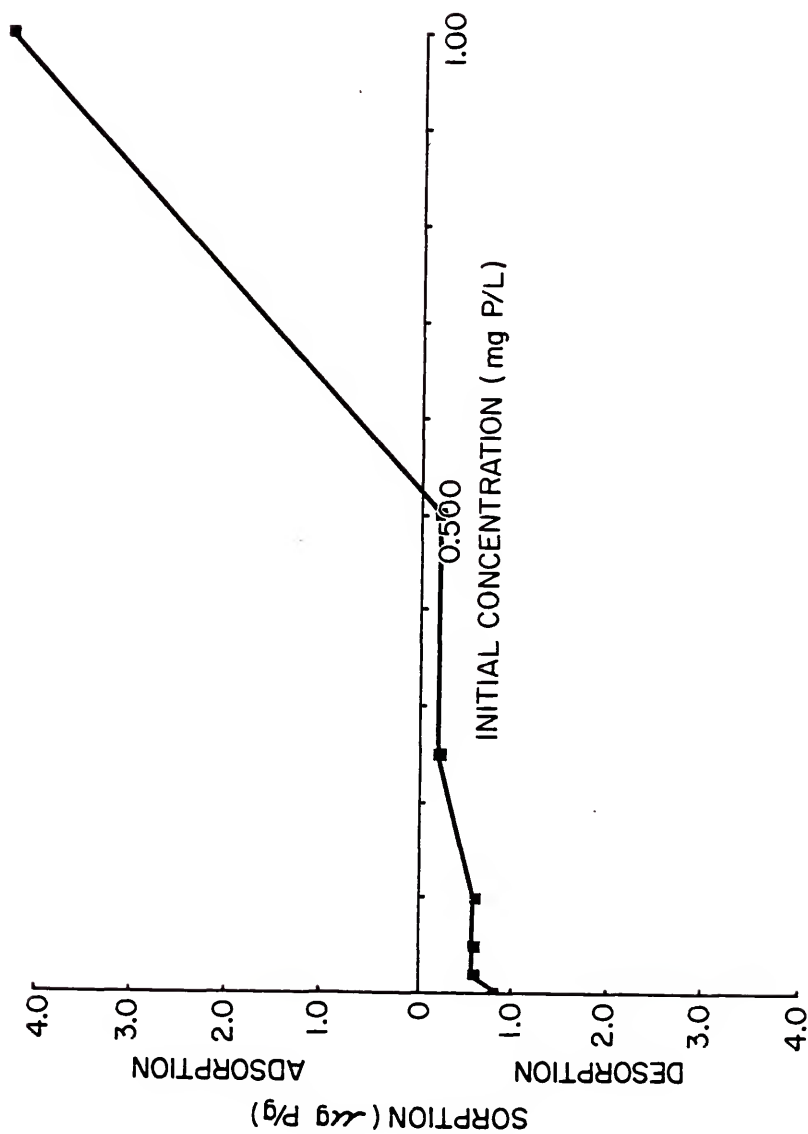


Figure V-4. SRP Sorption by Station 013 Sediments as a Function of Initial SRP Concentration.

indicate that these sediments have little affinity for phosphorus (Figure V-5).

Phosphorus sorption data for Lakes Okeechobee and Apopka sediments were evaluated for goodness of fit to the Langmuir adsorption isotherm model. This model was selected in favor of the Freundlich model, which has been widely used to describe phosphorus adsorption in solids and sediments (e.g., Carritt and Goodgal 1954; Fitter and Sutton 1975; Hwang et al. 1976; Pollman 1977). The Freundlich model is purely empirical, however, and it has no theoretical significance (Yariv and Cross 1979). The Langmuir model was derived by Langmuir (1918) from the kinetic theory of gases to describe gas adsorption on solids; it was applied to soils by Olsen and Watanabe (1957) and has been used extensively for lake sediments (e.g., Kuo and Lotse 1974; Edzwald 1977; Ku et al. 1978; Holm et al. 1979). Sposito (1979) applied statistical mechanics to verify the applicability of the Langmuir model to soils. The following section describes the assumptions inherent in the derivation of the Langmuir model and the implications of applying the Langmuir model to the prediction of adsorption and desorption processes.

Development of a Langmuir Sorption Model

The Langmuir model assumes that sorption is restricted to a monomolecular layer and that all sites are equally susceptible for sorption, i.e., the exchange sites are homogeneous with respect to surface energy. The Langmuir model can be written in the following linear form:

$$\frac{C}{\Gamma} = \frac{1}{b\Gamma_{\infty}} + \frac{C}{\Gamma_{\infty}} \quad (V-1)$$

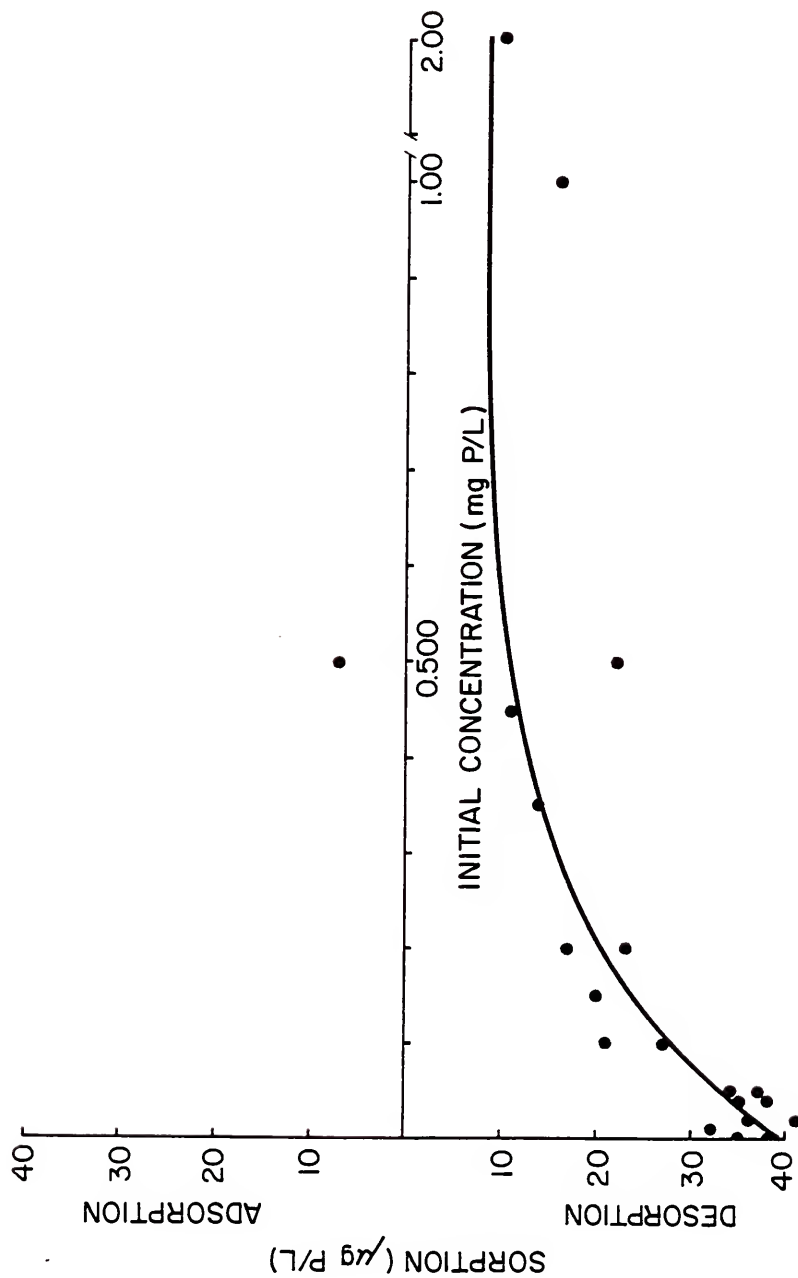


Figure V-5. SRP Sorption by Station A5 Sediment as a Function of Initial SRP Concentration.

where C = the equilibrium concentration of adsorbate (ug/L),
 Γ = the quantity of adsorbate adsorbed per unit mass of adsorbent (ug/g),
 Γ_{∞} = the adsorption capacity of the adsorbent (ug/g), and
 $b(L/ug)$ = a constant directly related to the binding energy.

Application of the Langmuir model to sorption phenomena has been restricted almost exclusively to describe adsorption. Theoretically, however, the model represents the synthesis of two competing processes, viz., adsorption and desorption, and thus can be employed to model desorption. This can be demonstrated by reviewing the derivation of the Langmuir equation for gaseous adsorption by solids. The isotherm can be developed on the basis of molecular kinetic theory which gives the number of molecules striking a unit surface area per unit time as (Jaycock and Parfitt 1981):

$$i = \frac{P}{(2\pi mkT)^{1/2}} \quad (V-2)$$

where P = the partial pressure of the gas or vapor of interest,
 m = the mass of an adsorbed molecule,
 k = Boltzmann's constant, and
 T = temperature.

Adsorption is restricted to a certain fraction, j , of molecules striking unoccupied surface sites. If the fraction of sites already occupied is ϕ (i.e., $\phi = N_a/N_s$ where N_s is the total number of exchange sites per unit surface area, and N_a is the number of sites occupied by adsorbed molecules), then the rate of adsorption is $ij(1-\phi)$.

Kinetic studies indicate that the rate of desorption per unit surface area and unit time will be $\phi N_s v \exp(-\psi/kT)$, where v is a constant of proportionality determining the probability of desorption, and ψ is the activation energy of desorption (Yariv and Cross 1979). The probability of desorption is thus $v \exp(-\psi/kT)$. At equilibrium the number of adsorbed molecules at the surface must be constant (i.e., the rate of adsorption equals the rate of desorption). Therefore

$$(1 - \phi) j P (2\pi mkT)^{-1/2} = N_s \phi v \exp(-\psi/kT) \quad (V-3)$$

This equation may be written as

$$\phi = \frac{bP}{1 + bP} \quad (V-4)$$

where $b = j (N_s \phi v \exp(-\psi/kT))^{-1} (2\pi mkT)^{-1/2}$.

Replacement of the equilibrium gas pressure with the equilibrium adsorbate concentration, C , and substituting the surface coverage, Γ , and the adsorption capacity, Γ_∞ , for N_a and N_s , respectively, gives

$$\frac{\Gamma}{\Gamma_\infty} = \frac{bC}{1 + bC} \quad (V-5)$$

or, alternatively

$$\frac{C}{\Gamma} = \frac{1}{b\Gamma_\infty} + \frac{C}{\Gamma_\infty} \quad (V-1)$$

Application of the Langmuir equation to predict the extent and direction of sorption (i.e., adsorption or desorption) can be developed as follows. Suppose a mass, m , of an adsorbing solid with an initial surface coverage of Γ_0 is introduced to a solution containing an

initial concentration, C_o , of adsorbate. At equilibrium, the adsorbate concentration in solution may be expressed as

$$C = C_o + \frac{\Delta x}{v} \quad (V-6)$$

where Δx = the net change of adsorbate mass in solution, and
 v = the solution volume.

Furthermore, conservation of mass requires that

$$\Gamma = \Gamma_o - \frac{\Delta x}{m} \quad (V-7)$$

The sign of Δx indicates the direction of sorption. If $\Delta x > 0$, then desorption occurs whereas adsorption is indicated if $\Delta x < 0$. Assuming that sorption is restricted to a monomolecular layer restricts the magnitude of adsorption such that

$$-\Delta x \leq m (\Gamma_\infty - \Gamma_o) \quad (V-8)$$

Furthermore, the extent of desorption cannot exceed the initial surface coverage of adsorbate

$$\Delta x \leq m \Gamma_o \quad (V-9)$$

With these constraints imposed, the change in equilibrium position of and C may be determined by substituting Equations V-6 and V-7 into the Langmuir equation

$$\frac{C_o + \frac{\Delta x}{v}}{\Gamma_o - \frac{\Delta x}{m}} = \frac{1}{b\Gamma_\infty} + \frac{C_o + \frac{\Delta x}{v}}{\Gamma_\infty} \quad (V-10)$$

Since all other parameters have been previously specified according to the initial conditions, only one variable, Δx , is unknown in the above equation.

Rearranging terms yields a quadratic expression which may be solved explicitly for Δx :

$$\frac{-b\Delta x^2}{m} + \Delta x \left(\frac{b\Gamma_o}{v} - \frac{1}{m} - \frac{bC_o}{m} - \frac{b\Gamma_\infty}{v} \right) + (\Gamma_o - bC_o\Gamma_\infty + bC_o\Gamma_o) = 0 \quad (V-11)$$

Depending upon C_o and Γ_o , no net sorption may occur. Under these conditions, which incidentally define the equilibrium adsorbate concentration (EAC), Δx equals zero.

From Equation V-11, it follows that the EAC (i.e., C_o at $\Delta x = 0$) is theoretically related to the number of unoccupied exchange sites

$$EAC = \frac{\Gamma_o}{b(\Gamma_\infty - \Gamma_o)} \quad (V-12)$$

Expressed in terms of fractional surface coverage, ϕ , Equation V-12 gives

$$EAC = \frac{1}{b} \frac{\phi}{1 - \phi} \quad (V-13)$$

Thus, according to the Langmuir relationship, complete coverage of all exchange sites (i.e., $\phi = 1$) is mathematically unattainable. Thus, complete surface coverage is approached asymptotically. Figure V-6 illustrates the variability of EAC as a function of ϕ for several different values of the Langmuir adsorption constant, b . The slope of

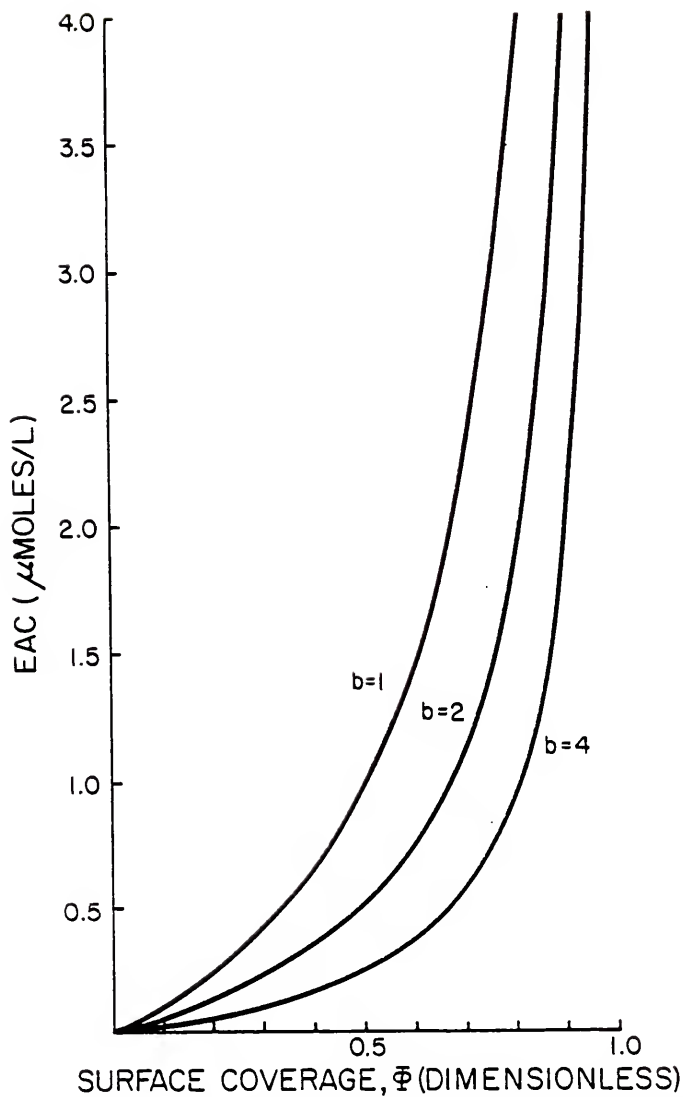


Figure W-6. Theoretical Relationship Between Equilibrium Adsorbate Concentration (EAC) (μmole/L) and Fractional Surface Coverage, Φ , for Various Values of the Langmuir Adsorption Constant, b (L/μmole).

the curve is a measure of the buffering capacity of the system. More explicitly, when surface coverage (ϕ) is low, EAC is restricted to a relatively narrow (and low) concentration range; as ϕ increases, the ability of the adsorbate-adsorbent system to buffer against perturbations (e.g., introduction of additional solute) decreases according to the following equation:

$$\frac{d \text{ EAC}}{d\phi} = \frac{1}{b (1 - \phi)^2} \quad (\text{V-14})$$

The relationship also illustrates the influence of b on the buffering capabilities of the system. The slope of change in EAC relative to ϕ is an inverse function of b ; thus as b increases, concomitant increases in buffering capacity result (Figure V-6). By definition, however, b is invariant for a particular surface; a change in b thus represents a change in system conditions (e.g., pH or temperature) or surfaces.

In using the Langmuir relationship to interpret sorption phenomena near or below the EAC, it is critical that the initial surface coverage Γ_0 be accounted for. Failure to include Γ_0 renders Equation V-10 indeterminate at the EAC when no net sorption is observed.

The effect of excluding Γ_0 may be evaluated by considering a model system comprising 1 g of adsorbent, Γ_0 equal to 125 $\mu\text{g/g}$, Γ_∞ equal to 1,000 $\mu\text{g/g}$, b equal to 1/2625, and a solution volume of 1 liter. Table V-1 summarizes calculations for C/Γ values for a series of different initial adsorbate concentrations in solution, including both values for C/Γ corrected for initial surface coverage, Γ_0 (i.e., actual C/Γ , where $\Gamma = \Gamma_0 - \Delta x/m$), and excluding Γ_0 (i.e., apparent C/Γ ,

Table V-1. Apparent and Corrected C/Γ Values for a Model Adsorbate-Adsorbent System for Varying Initial Concentrations of Adsorbate. (See text for specification of Langmuir constants and system dimensions.)

Initial Concentration (ug/L)	$\Delta x/v$ (ug/L)	Final Concentration (ug/L)	Apparent C/Γ (g/L)	Corrected C/Γ (g/L)
0	91.4	91.4	-1.00	2.72
50	78.4	128	-1.64	2.75
100	65.6	166	-2.52	2.79
150	53.2	203	-3.82	2.83
250	28.9	279	-9.65	2.90
375	0	375	*	3.00
500	-27.5	473	17.2	3.10
1,000	-125	875	7.00	3.50
1,500	-205	1,295	6.31	3.92
2,000	-272	1,728	6.35	4.35
2,500	-328	2,172	6.63	4.80

* Indeterminate.

where $\Gamma = -\Delta x/m$). Plotting actual C/Γ versus equilibrium or final concentrations generates the typical Langmuir plot in accordance with Equations V-1 and V-10 (Figure V-7). At an initial concentration of 0 ug/L of adsorbate, a net release of 91.4 ug adsorbate is calculated; thus, the isotherm extends linearly from a lower limit of C/Γ equal to 2.72. Plotting apparent C/Γ versus C shows that at concentrations above, but approaching the model becomes increasingly unstable; at concentrations well beyond the EPC, C/Γ approaches its true value asymptotically with increasing C .

Failure to correct Γ for initial surface coverage not only leads to spurious values of adsorption parameters, but may result in the misinterpretation of observed sorption phenomena. This is evidenced by the work of McAllister and Logan (1978) and Green et al. (1978) who described the phosphorus adsorption-desorption characteristics of soils and sediments derived from the Maumee River basin in Ohio. Adsorption was described by the Langmuir model, although the authors apparently neglected to correct for initial surface coverage. Their results show what the authors described as a characteristic "check-mark" shaped curve which closely parallels the curvilinear relationship obtained by plotting apparent C/Γ versus C . The authors hypothesized that the apparently anomalous departure from linearity near the equilibrium phosphorus concentration (EPC) reflects the strong buffering capacity of the system against increases in phosphorus concentration. Although buffering capacity does increase with decreasing concentration, such a mechanism is implicitly contained within the Langmuir model and does not result in a deviation from linearity. Similar analytical anomalies near

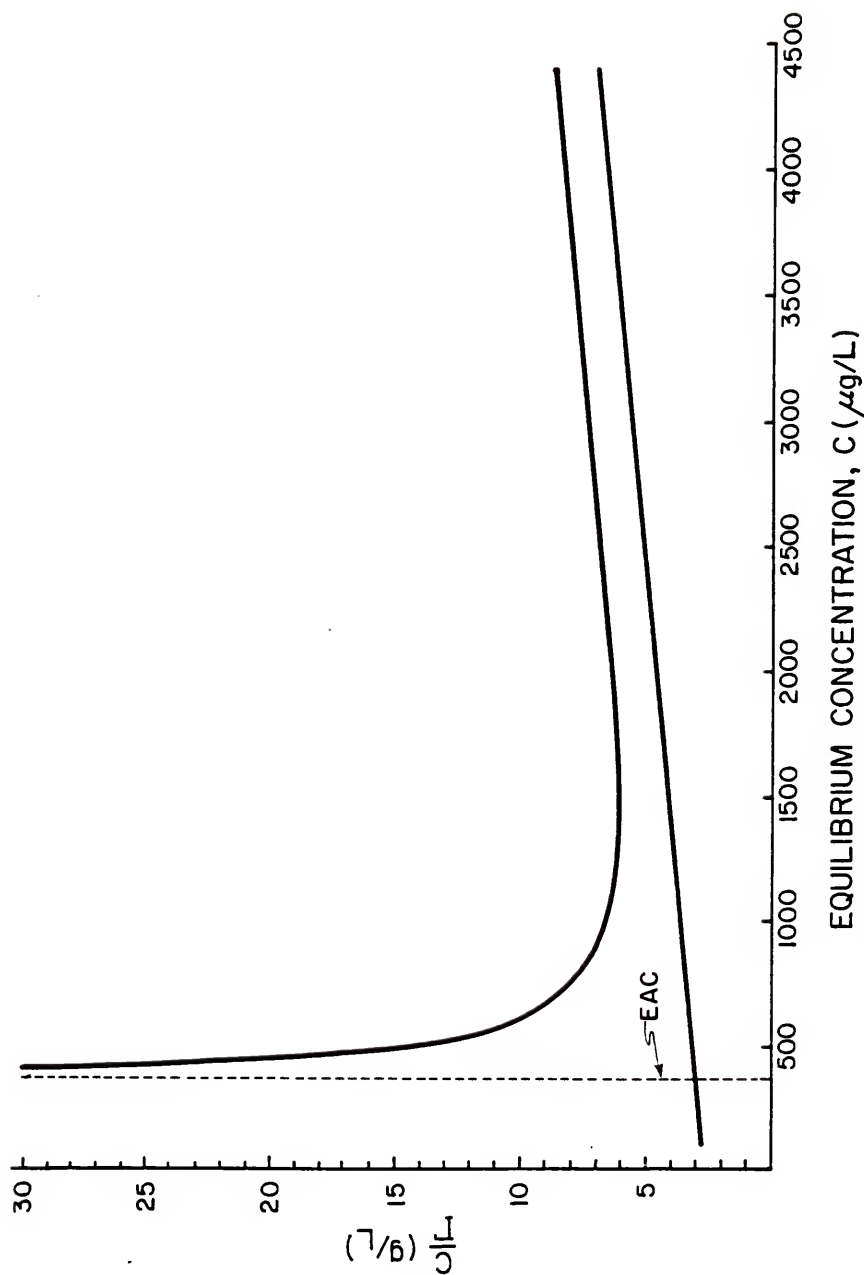


Figure V-7. Langmuir Plot of Apparent and Corrected C/T Versus Equilibrium Concentration for Model Adsorbate-Adsorbent System. See Text for Specification of Langmuir Constants and System Dimensions.

and below the EPC have been alluded to by Fitter and Sutton (1975) in fitting experimental sorption isotherms to the Freundlich model.

Application of Langmuir Model to Lake Apopka
and Lake Okeechobee Sediments

Sorption by sediments from Stations A5, 010, 011, and 013 was well described by the Langmuir model; correlation coefficients for the model were highly significant ($p < 0.01$) and exceeded $r = .97$ (Table V-2; Figures V-8 and V-9). Sediments from Stations 07 and 014 showed poor agreement between observed results and the model, particularly at concentrations below the EPC. Both sediments showed a pronounced tendency at low initial P concentrations to buffer sediment-water suspensions at equilibrium concentrations approximating 160 to 170 ug P/L (Figures V-10 and V-11). The observed deviations at low equilibrium P levels may indicate error introduced by underestimation of the initial (calculated) surface concentration. Adsorption maxima for Lake Okeechobee sediments varied with sediment type, ranging from 6.5 ug/g for Station 013, which primarily comprises quartz sands, to 229 ug/g for the organic sediments of 014. Adsorption maxima for Lake Okeechobee sediments were significantly correlated ($r^2 = .96$, $p < 0.05$) with sediment fractional silt-clay content. With the exception of Stations 07 and 014, the observed adsorption maxima constitute some of the lowest values reported in the literature (Table V-3). These results suggest that adsorption maxima are controlled by substrate type (Stumm and Leckie 1971). Edzwald et al. (1976) determined, for example, that solid silica has no capacity to adsorb phosphorus. Conversely, clay

Table V-2. Summary of Langmuir Sorption Parameters and Goodness of Fit to Model for Lake Okeechobee and Lake Apopka Sediments (pH 8.30).

Sample	NAI-P (ug P/L)	Γ_{∞} (ug P/g)	b (x 10 ³) (L/ug)	EPC* (ug P/L)	r	P (Probability)
011	35	91.0	7.51	83.2	.982	<0.01
010	12	27.4	4.29	181	.982	<0.01
013	6	6.5	20.8	577	.970	<0.01
014	96	228.6	1.74	416	.719	†
07	66	**	**	**	**	†
A5	108	108.4	34.6	7,190	.999	<0.01

* Calculated.

† P > 0.05.

** Not included because of lack of significant data.

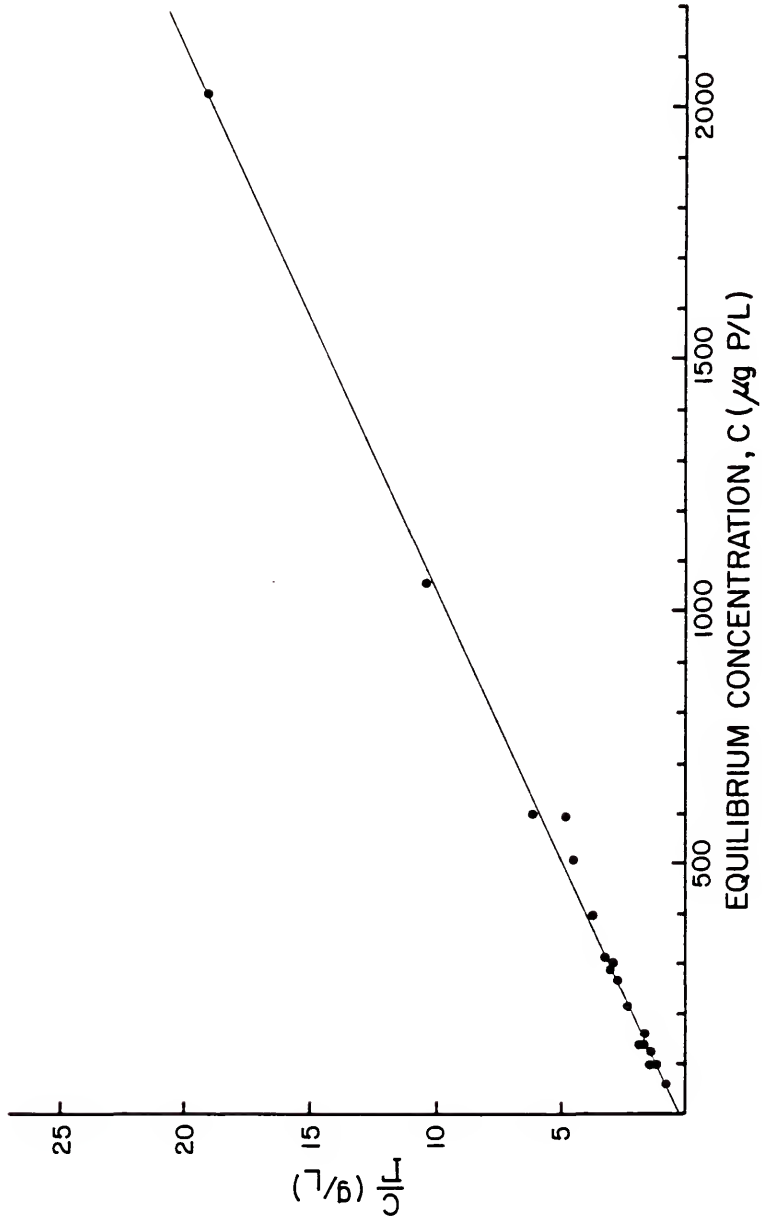


Figure V-8. Langmuir Sorption Isotherm Plot for Lake Apopka Sediment (Station A5).

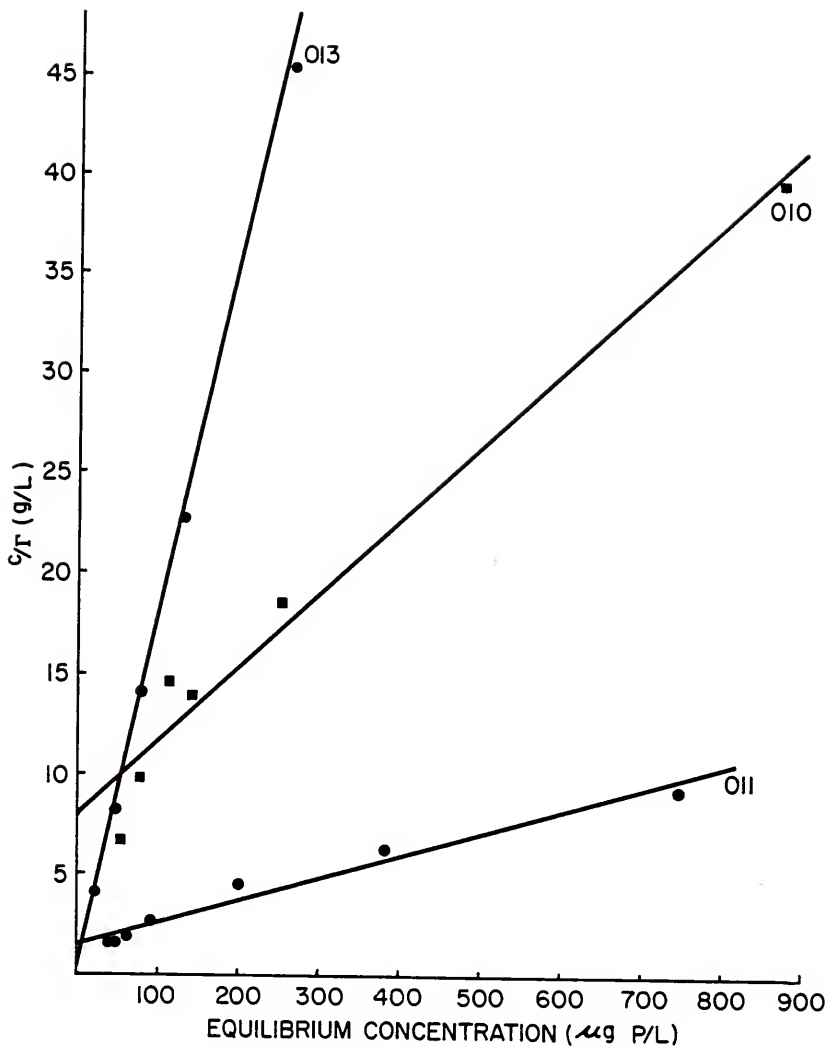


Figure V-9. Langmuir Sorption Isotherm Plot for Lake Okeechobee Sediments (Stations 010, 011, and 013).

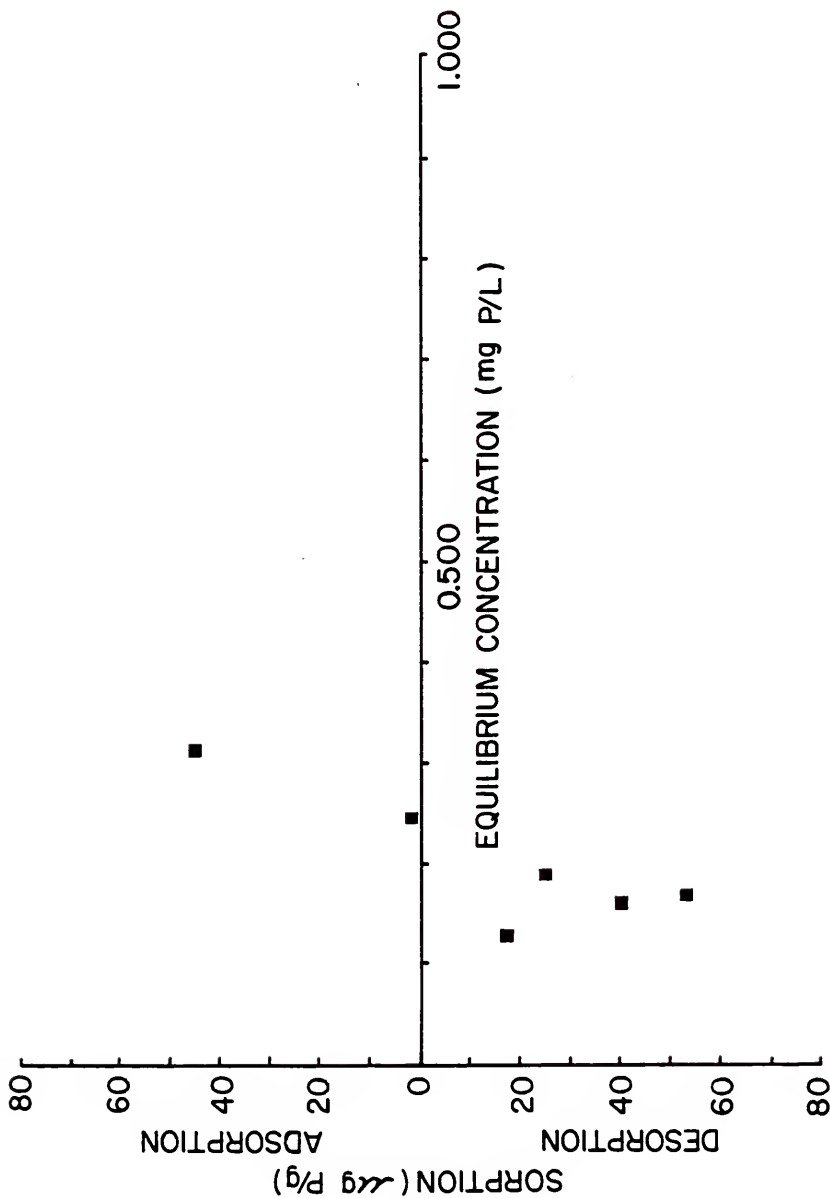


Figure V-10. SRP Sorption by Station 07 Sediments as a Function of Final (equilibrium) Concentration.

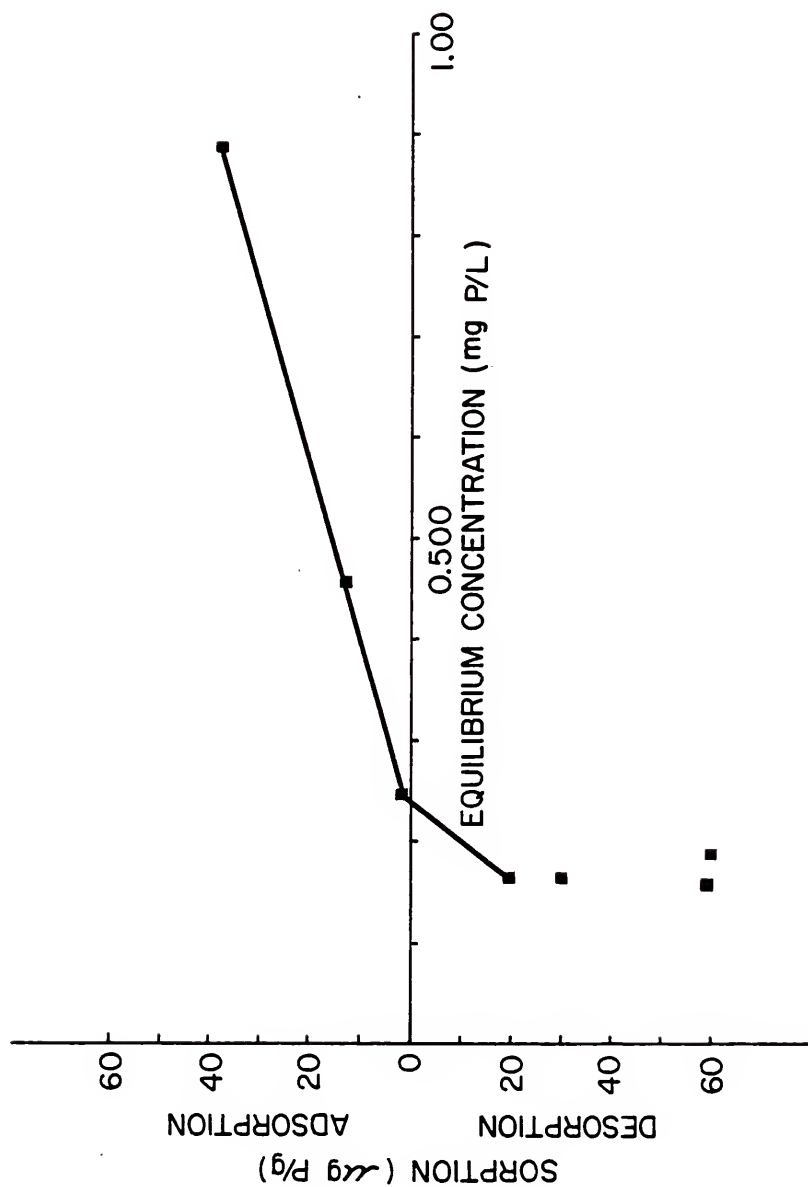


Figure V-11. SRP Sorption by Station 014 Sediments as a Function of Final (equilibrium) Concentration.

Table V-3. Values of Langmuir Sorption Parameters for Phosphate Sorption by Different Substrates.

Substrate Type/Source	$b(L/\mu g) \times 10^3$	Γ_{∞} ($\mu g/g$)	Reference
Sao Gabriel	4.8	73	Syers et al. 1973
Cambal	4.7	224	Syers et al. 1973
Durox	10.9	990	Syers et al. 1973
Pierre Clay	0.45	255	Olsen and Watanabe 1957
Owyhee Silt Loam	0.31	136.3	Olsen and Watanabe 1957
Calcite	--	9.17	Griffin and Jurinak 1973
Lake Warner	1.06	1,125	Ku et al. 1974
Lake Wyola	1.26	1,209	Ku et al. 1974
Maumee River Basin	0.68- 1.55	222- 4,870	McAllister and Logan 1978
Menominee River	2.15	282	Holm et al. 1979
Kaolinite #3	--	91	Edzwald et al. 1976
Montmorillonite #21	--	746	Edzwald et al. 1976
Illite #36	--	2,510	Edzwald et al. 1976

substrates, and in particular 2:1 clays, have relatively high adsorptive capacities for phosphorus (e.g., Edzwald et al. 1976, Table V-3).

Since particle surface area increases with decreasing particle size, a conjugate interpretation of these results is that the extent of adsorption is controlled by particle surface area. Olsen and Watanabe (1957) previously demonstrated the functional dependency of adsorption maximum on surface area for both acidic and alkaline soils.

Krom and Berner (1980b) evaluated P adsorption in anoxic estuarine sediments in terms of a simple distribution coefficient, K^* , that relates adsorption to equilibrium concentration in a linear fashion:

$$\Gamma = K^* C \quad (V-15)$$

This equation can be derived from the Langmuir model under the limiting condition that the inverse of the adsorption constant, $1/b$, greatly exceeds C . If this condition is not met, then K^* will vary inversely with increasing concentration. An advantage of Equation V-15 is that it provides direct information about sediment buffering capacity; i.e., the greater the distribution coefficient, the more pronounced the affinity of the substrate for the solute. Distribution coefficients for a variety of substrate types were summarized by Krom and Berner (see Table V-4). The relatively high adsorption energies of Lake Okeechobee and Lake Apopka sediments precludes use of Equation V-15, except at extremely low concentrations. K^* decreases with increasing C because the high energy binding sites quickly become saturated. An example of the decrease in K^* (and thus in buffer capacity) with increasing C is presented for Lake Okeechobee Station 013 in Figure V-12.

Table V-4. Values of Mass of Phosphate Adsorbed/Equilibrium Concentration for Different Substrates. (Data should be used for approximate comparisons. Experimental conditions varied between studies and often data have been fitted to nonlinear isotherms.)

Substrate	Oxygen Status in Experiment	K*	Reference
Iron oxide (goethite)	oxic	3,000	Hingston et al. 1974
Illite	oxic	250	Edzwald et al. 1976
Montmorillonite	oxic	100	Edzwald et al. 1976
Kaolinite	oxic	20	Edzwald et al. 1976
Calcium carbonate (syn. powder)	oxic	20	Cole et al. 1953
Calcite	oxic	10	de Kanel and Morse 1978
Aragonite	oxic	175	de Kanel and Morse 1978
Soil	oxic	15-70	Olsen and Watanabe 1957
Soils	oxic and anoxic	80	Khalid et al. 1977
Lake sediment	oxic	40	Hwang et al. 1976
Lake sediment			
Calcareous	oxic	35	Li et al. 1972
Noncalcareous	oxic	25-35	Li et al. 1972
Lake Sediment			
Calcareous	anoxic	6	Li et al. 1972
Noncalcareous	anoxic	1-5	Li et al. 1972
Estuarine sediment	oxic	3,750	Jitts 1959
Estuarine sediment	oxic	250	Pomeroy et al. 1965
Estuarine sediment	oxic	50	Krom and Berner 1980a
Oceanic sediment	oxic	500-5,000	Berner 1973
Estuarine sediment	anoxic	1	Krom and Berner 1980b

Source: Krom and Berner 1980a.

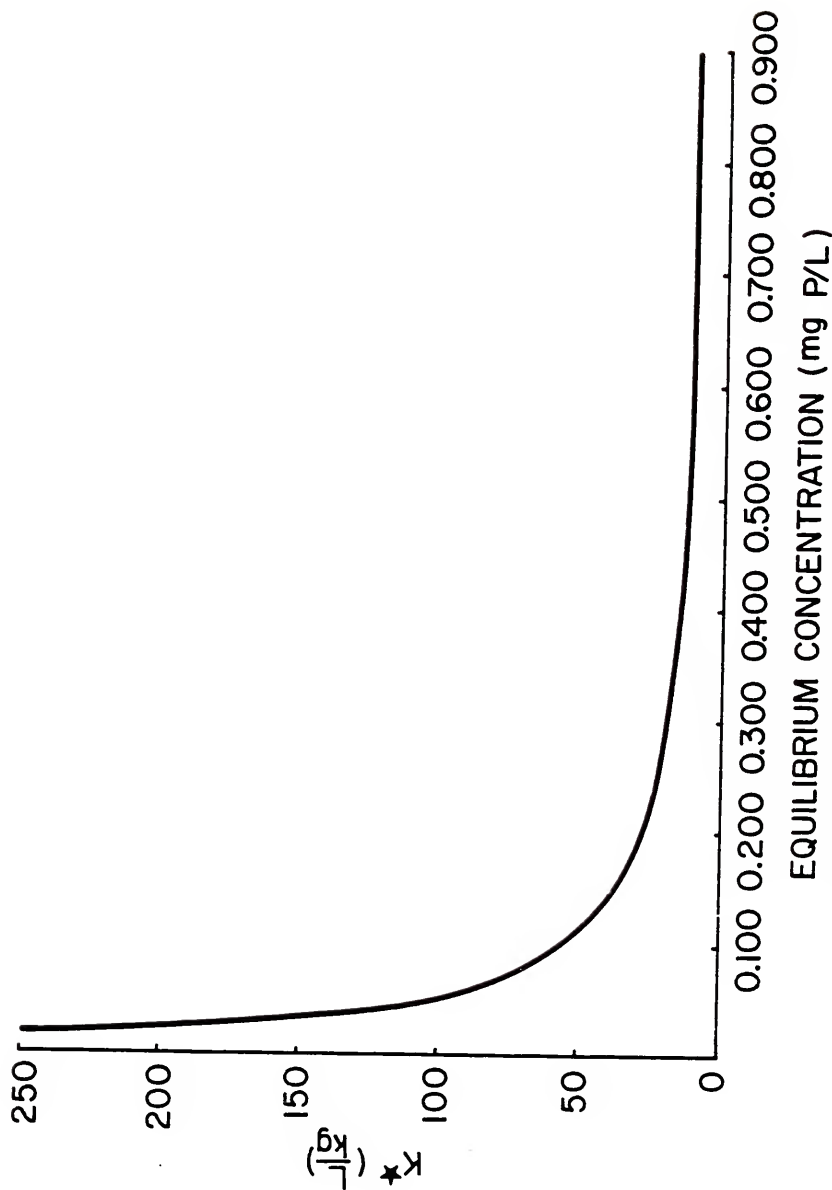


Figure V-12. Variation of the Phosphorus Mass Distribution Coefficient, K^* , Related to Equilibrium Concentration Levels of Phosphorus for Station 013 Sediments.

Equilibrium Phosphorus Concentration (EPC)

By definition, the EPC indicates the direction of sorption response when a sediment particle is resuspended and brought into contact with the overlying water column. Release or uptake occurs as the solid phase equilibrates with the aqueous phase (which generally has a dissolved phosphorus level different from that of the interstitial solution with which the sediment particle had originally equilibrated). EPC values observed for Lake Okeechobee sediments were rather variable (Table V-5), ranging from 80 ug P/L to 520 ug P/L. Mean annual SRP concentrations at various locations throughout Lake Okeechobee between 1973 and 1979 never exceeded 58 ug P/L (Federico et al. 1981); thus Lake Okeechobee sediments will function as a nutrient source if resuspended. EPC levels for Lake Okeechobee sediments correspond to EPCs observed for other Florida lakes; for example, Nisson (1975) observed EPC values ranging from 80 to 2,000 ug P/L for Lakes Harney, Jessup, and Monroe. EPC values as low as 2 ug P/L have been reported by Meyer (1979) for Bear Brook in the Hubbard Brook watershed. McAllister and Logan (1978) and Mayer and Gloss (1980) also observed somewhat lower EPC levels than those found for Florida lakes. Reported values for bottom sediments ranged respectively from 24 to 54 ug P/L (Maumee River, Ohio) and 15 and 70 ug P/L (Colorado River, Utah).

EPC for the Lake Apopka sediment was quite variable and difficult to define accurately. Figure V-5, which represents the synthesis of two separate adsorption-desorption experiments, indicates EPC values of 470 ug P/L and approximately 2,000 ug P/L. Between 1977 and 1980, lakewide monthly average SRP concentrations for Lake Apopka were always

Table V-5. Observed and Calculated EPC (ug P/L) Values for Lake Okeechobee and Lake Apopka Sediments (pH 8.30).

Station	ϕ	Observed EPC (ug P/L)	Calculated EPC (ug/L)
07	*	225	*
010	0.438	217	181
011	0.385	80	83
013	0.923	520	577
014	0.420	230	417
A5	0.996	470-2,000	7,190

* Not calculated.

below 200 ug P/L; thus the net direction of sorption upon sediment resuspension will be release of SRP to the water column. Although the broad disparity between measured EPC values was initially surprising, the observed variance is consistent with the inherent decrease in buffering capacity predicted by the Langmuir model as surface coverage approaches complete saturation. As described previously (Equation V-13), EPC is theoretically an inverse function of the number of exchange sites unoccupied by phosphate anions.

Using this relationship described by Equation V-13, predicted EPC as a function of fractional surface coverage for Station A5 sediment is plotted in Figure V-13. Initial surface coverage was estimated at 108 ug P/g compared with an adsorption maximum of 108.4 ug P/g (Table V-2); ϕ consequently assumes a value of 0.996 and EPC is predicted to be 7,200 ug P/L. As evidenced by Figure V-13, EPC is highly sensitive in this range to small changes in surface coverage (and hence ϕ); for example, a decrease in Γ of only 2 ug P/g yields ϕ equal to 0.978 and a predicted EPC of 1,280 ug P/L. A further reduction in Γ to 102 ug/g results in a predicted EPC of 461 ug P/L. Because the capacity of these sediments to further adsorb phosphorus is virtually exhausted, interstitial water concentrations of SRP are highly variable and can reach quite elevated levels. Above ϕ equal to approximately 0.85, larger increases in SRP concentrations are required to effect even a small increase in Γ . Thus, despite their limited ability to buffer against increases in interstitial SRP concentrations, the sediments exert a profound influence in maintaining SRP concentrations at high levels. For example, the minimum equilibrium SRP concentration in the

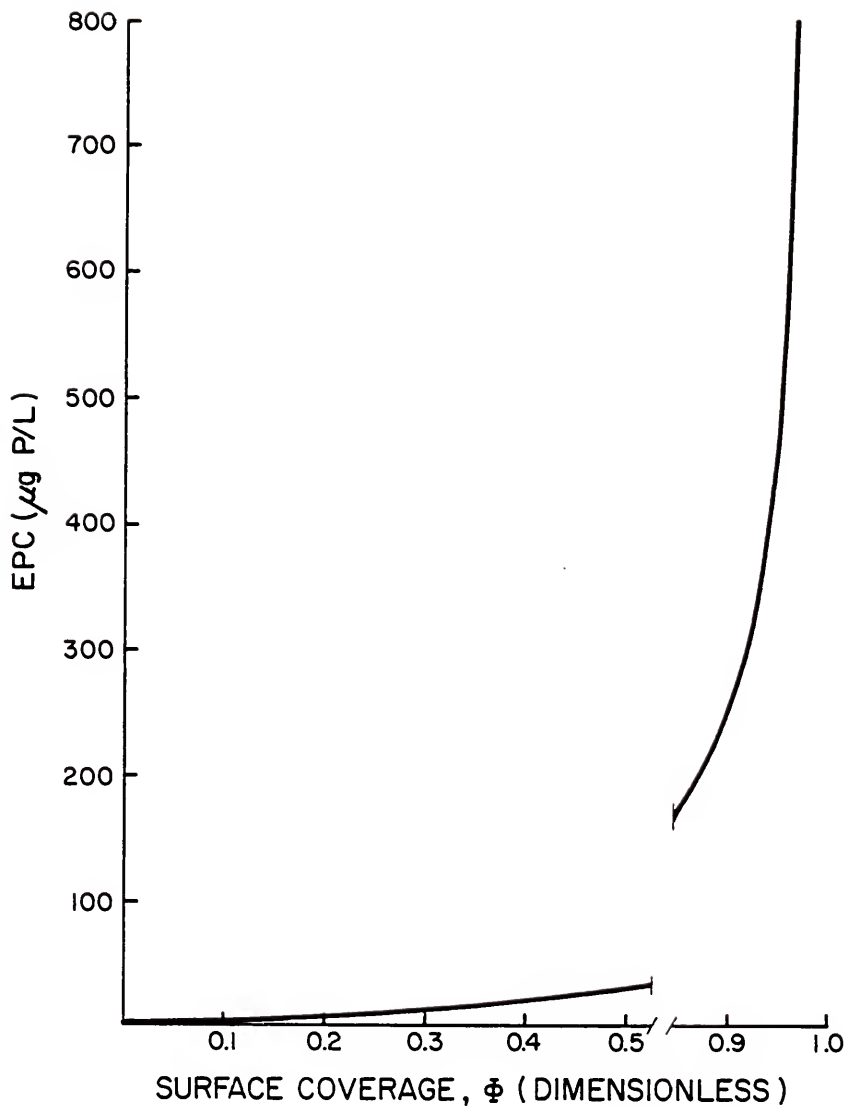


Figure V-13. Theoretical Relationship Between Fractional Surface Coverage (Φ) and EPC for Station A5 Sediments.

pore fluid of Station A5 sediments can be calculated as follows. The sediments are characterized by a particulate density of 1.935 g/cm^3 and an average water content of 96.5 percent. Assuming that the interstitial fluid has no dissolved phosphorus as an initial condition (a situation which is approximated when overlying water of low SRP concentration is buried along with newly deposited sediment particles), application of Equation V-11 predicts an equilibrium interstitial fluid SRP concentration of 233 ug P/L when Γ_o equals 108 ug P/g.

Regression analysis was performed to determine whether EPC is a linear function of labile inorganic P content (NAI-P), and results indicate that these two parameters are not significantly correlated ($r^2 = .14$, $p > 0.05$). McAllister and Logan (1978) had a similar lack of success in correlating Bray P1 "available" P with EPC in sediments from the Maumee River. The lack of correlation between EPC and NAI-P directly follows from the theoretical relationship between EPC and ϕ described by Equation V-13. The relationship is valid if the model is restricted to a single sediment and if all binding sites are energetically homogeneous (i.e., b is invariant). Because the adsorption constant (b) varies with sediment type, a simple correlation between $\phi/1-\phi$ and EPC for different sediments is not likely to exist. Indeed, such a correlation for Lake Okeechobee sediments yielded a rather poor relationship ($r^2 = .52$). Green et al. (1978) and McAllister and Logan (1978) empirically demonstrated a negative correlation between EPC and adsorption energy; similarly, Holford (1978) indicated that ease of desorption (and implicitly EPC) is inversely related to the binding energy.

Desorption

The greatest magnitude of desorption from Lake Okeechobee sediments was observed for sediments from Stations 07 and 014. At initial aqueous concentrations of 0 ug P/L, these two sediments released 52.9 ug P/g and 52.6 ug P/g sediment, respectively (corrected for interstitial P content). Release from other Lake Okeechobee sediments was substantially lower under the same initial conditions and ranged from 0.8 ug P/g (Station 013) to 8.1 ug P/g (Station 011). Desorption from Lake Apopka was relatively moderate, with an average observed release of 25.4 ug P/g. Williams et al. (1970) observed that sediments with the highest adsorptive capacity usually release the least P in subsequent desorption experiments. The converse is true for the sediments evaluated in this study; the most pronounced release was observed in the sediments with the greatest adsorptive capacities (Stations A5, 07, and 014). The results of Williams et al. (1970) cannot be extrapolated directly to Lake Okeechobee sediments because of the broad disparity in sorptive characteristics between the major sediment types.

A more useful parameter indicative of the ease of desorption is obtained from the fraction of the initial surface coverage (NAI-P) that can be readily desorbed. Release of surface sorbed P is more easily induced from Stations 07 and 014 sediments than from other sediments (Table V-6). A comparison of Langmuir binding constants and fractional desorption suggests that release is inversely related to bonding energy (Figure V-14). This relationship may be described by the following empirically derived model ($r = .815$):

Table V-6. Desorption Characteristics of Lake Okeechobee and Lake Apopka Sediments in Buffered (pH 8.30), Phosphorus-Free Water.

Sample	NAI-P (ug P/g)	Release (ug P/g)	Fractional Release (dimensionless)	b(L/ug) x 10 ³
07	65	52.9	0.81	*
010	12	4.0	0.33	4.59
011	35	8.1	0.23	7.51
013	6.0	0.8	0.13	20.9
014	96	52.6	0.55	1.74
A5	108	25.4	0.24	34.6

* Not calculated.

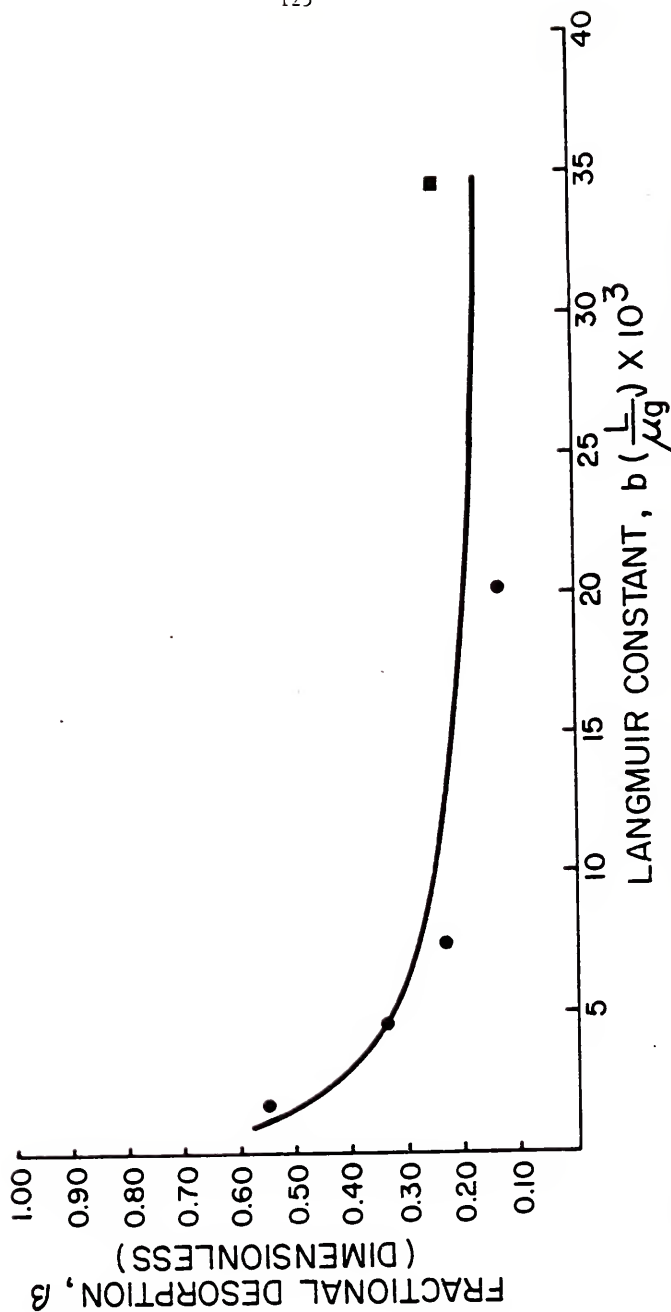


Figure V-14. Relationship Between Fractional Desorption, β , and Langmuir Binding Constant, b , for Lake Okeechobee (●) and Lake Apopka (■) Sediments.

$$\beta = 0.0472 b^{-0.361}$$

(V-16)

where β = the fraction of labile P desorbed.

These results concur with those of Holford and Mattingly (1976) and McAllister and Logan (1978), who demonstrated an inverse relationship between the ease of desorption of labile P and bonding energy. Desorbed P probably represents low-energy, electrostatically-bound P, as opposed to specifically sorbed P (Hingston et al. 1976; Obihara and Russel 1972; and Kuo and Lotse 1974). Williams et al. (1970) found that calcareous sediments generally release greater fractional quantities of adsorbed P than do noncalcareous sediments; furthermore, the adsorption data of Holford and Mattingly (1975) indicate that carbonate particles have lower bonding energy sites than do iron hydrous oxides.

For sediments characterized by both relatively high water content and interstitial SRP concentrations, entrainment of pore fluid during sediment resuspension complements desorption as a significant mechanism of phosphorus release. For example, at an initial aqueous concentration of 0 ug P/L, net release from Station A5 sediment averaged 36.5 ug P/g; of this total, 30 percent was directly the result of entrained pore fluid. In Lake Okeechobee sediments, which are generally characterized by lower sedimentary water contents and lower pore fluid concentrations of SRP (Table III-1), this mechanism is for the most part insignificant. Station 014 sediments are somewhat anomalous with respect to this general rule; even so, entrainment of pore fluid accounts for less than 12 percent of the observed total release.

Effect of pH on P Sorption by Lake Okeechobee and Lake Apopka Sediments

An experiment was conducted to evaluate the influence of pH on sorption phenomena. Adsorption-desorption isotherms were conducted on sediment from Station 014 at pH 7.20, 8.30, and pH 9.30 and from Station A5 at pH 7.10, 8.30, and 9.30 to bracket the observed variability of pH in Lakes Okeechobee and Apopka. The results (Figures V-15 and V-15a) indicate that minimum desorption for both sediments occurs at pH 8.3; pH shifts in either direction enhance desorption. Increased desorption at pH 7.10 to 7.20 probably reflects dissolution of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) or other calcium phosphate solid phases. This mechanism does not explain the increase of P release at pH 9.30. Specific adsorption of P is inhibited by increasing hydroxide concentration (Atkinson et al. 1974; Lijklema 1977 and 1980; Hingston et al. 1967); consequently, the functional response of desorption with varying pH in Lake Okeechobee and Lake Apopka sediments appears to represent a compromise between the decreasing solubility of hydroxyapatite (or other Ca-P phases) with increasing pH and enhanced competition of hydroxide ions for exchange sites.

The variability of EPC with pH is more complex and difficult to interpret, with different trends observed for the two sediments. As seen in Figure V-15b, the distribution of EPC with pH for Station A5 sediment is precisely the inverse of the observed change in desorption; EPC shows a pronounced maximum (470 to 2,000 ug P/L) at pH 8.3 contrasted with minimal desorption of the same pH. These results are contrary to a priori expectations; that is for sediments that conform to the Langmuir model, implicit in an increase in EPC is greater ease of

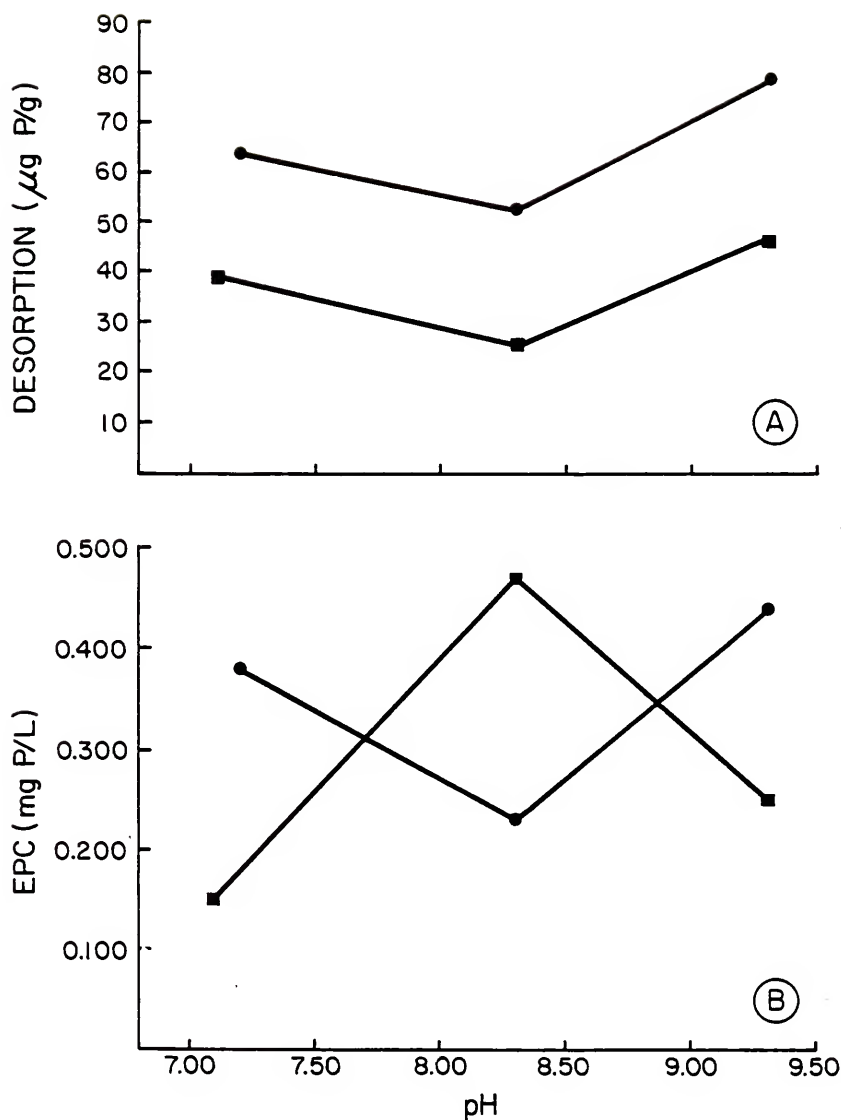


Figure V-15. Phosphorus Desorption ($\mu\text{g P/g}$) (A) and EPC (mg P/L) (B) as a Function of pH for Station A5 (\bullet) and 014 (\blacksquare) Sediments.

desorption. This follows from Equation V-13, which shows that increases in EPC are a direct consequence of increases in the extent of relative surface coverage ϕ . In addition, Equation V-11 demonstrates that the magnitude of desorption increases with increasing Γ_0 (implicitly ϕ) and/or decreasing b . Comparison of calculated Langmuir constants for Station A5 sediment at different pH shows that the adsorption b at pH 7.10 is reduced by more than 50 percent relative to pH 8.3 (Table V-7). However, the adsorption maximum, Γ_∞ , is substantially higher at pH 7.10, resulting in a predicted EPC of 174 ug P/L. This predicted value agrees rather well with the observed EPC of 150 ug P/L.

Furthermore, the increase in Γ_∞ agrees conceptually with results of Hingston et al. (1967), who demonstrated that the adsorption maximum of a particular surface for polybasic acids such as phosphoric acid increases with decreasing pH. This effect is attributed to a change in speciation of the anion resulting in less development of a negative charge by the surface upon specific adsorption of the anion. The net result is, therefore, an effective increase in the anion exchange capacity of the sediment. The observed decrease in EPC at pH 9.30 (relative to pH 8.30) can not be explained in terms of the Langmuir model and, as evidenced by the poorer fit of the Langmuir model to the experimental data ($r^2 = .729$, Table V-7), probably represents heterogeneous nucleation with calcite or precipitation as hydroxyapatite (Stumm and Leckie 1971; Griffin and Jurinak 1974).

EPC variability with pH for Station 014 sediment parallels the variability of maximum desorption (Figure V-15). The minimum EPC (230 ug P/L) was observed at pH 8.30; shifts in pH in either direction

Table V-7. Calculated Langmuir Constants for Station A5 Sediment as a Function of pH.

pH	Γ_{∞} (ug P/g)	$b(L/ug) \times 10^3$	r^2
7.10	149.9	14.8	.972
8.30	108.4	34.6	.999
9.30	108.2	8.51	.729

result in corresponding increases in EPC. The lack of fit of the sorption data to the Langmuir model precludes its use in interpreting the results and suggests that other mechanisms in addition to sorption contribute to the observed results.

Development of a Sediment Resuspension Phosphorus Release Model
for Lake Okeechobee and Lake Apopka

Nutrient Release Submodel

From the Langmuir relationship, a nutrient release submodel applicable to sediment resuspension can be developed to predict P release and equilibrium P concentrations as a function of initial conditions. From mass-balance considerations, the equilibrium concentration of phosphorus in a sediment-water suspension, C , is equivalent to

$$C = C_o + \frac{\Delta x}{V} \quad (V-6)$$

where C_o = initial concentration (ug/L) in the water column,

Δx = amount of P desorbed (ug), and

V = volume of lake water under consideration (L).

Since C_o can be specified, the solution to this equation requires the determination of Δx , which in turn may be solved from the following quadratic expression derived previously from the Langmuir model:

$$\frac{-b\Delta x^2}{m_s V} + \Delta x \left(\frac{b\Gamma_o}{V} - \frac{1}{m_s} - \frac{bC_o}{m_s} - \frac{b\Gamma_\infty}{V} \right) + (\Gamma_o - bC_o\Gamma_\infty + bC_o\Gamma_o) = 0 \quad (V-11)$$

where m_s = amount of sediment resuspended (g).

If the concentration of resuspended sediment is known, the derived Langmuir coefficients and this information can be used to predict the extent of release and hence, the final (equilibrium) aqueous phase concentration.

Sorption behavior observed in sediments from Lake Apopka (Station A5) and Stations 010, 011, and 013 from Lake Okeechobee agreed extremely well with the Langmuir model (Table V-2); consequently, the above model can be employed to predict equilibrium aqueous phase P concentrations resulting from the resuspension of these sediments. The poor fit of the Langmuir model to data for Stations 07 and 014, however, necessitates the use of a different model. The curvilinear response of sorption to increasing initial concentration for these sediments precludes the application of linear models; consequently, a series of nonlinear empirical models were evaluated through least squares analysis for adequacy of fit. Sorption data for Station 014 sediments were found to closely fit ($r^2 = .989$; $p < 0.01$) a logarithmic model:

$$\frac{\Delta x}{m_s} = -120.1 + 22.2 \ln C_o \quad (V-17)$$

An equivalent model applied to sorption data for Station 07 sediments yielded a poorer fit ($r^2 = .865$), but these data were described adequately by the following quadratic model ($r^2 = .976$; $p < 0.01$):

$$\frac{\Delta x}{m_s} = -43.6 + 0.221 C_o - 9.10 \times 10^{-5} C_o^2 \quad (V-18)$$

Because of the characteristics of a quadratic curve, use of this model at initial concentrations approaching and exceeding 1,200 ug P/L will introduce significant error. A potential source of error in this approach is that sorption is assumed to be independent of the solids/solution ratio; however, Hope and Syers (1976) concluded that this error is not significant if equilibrium is established.

Sediment Resuspension Model

The oscillatory motion of water under wave action generates a stress, τ_o , at the sediment-water interface that will induce scour or resuspension if a critical threshold stress, τ_c , is exceeded. Once particle motion has been initiated from the sediment surface, the rate of erosion is a function of the wave-induced stress in excess of the critical shear stress (Sternberg 1972; Sheng and Lick 1979; Fukuda 1978); for example

$$J = fct(\Delta\tau) \quad (V-19)$$

where $\Delta\tau = \tau_o - \tau_c$, and

J = the flux of sediment.

The magnitude of τ_o depends on prevailing wind conditions and associated wave parameters; τ_c depends on the sediment physical characteristics. Development of a physical sediment resuspension model thus can be viewed as comprising three distinct subunits: (1) determination of wind-induced stress, (2) evaluation of the critical stress for a particular substrate type, and (3) prediction of the sediment

flux. Once developed, the model can be interfaced with a nutrient-release submodel to predict water column phosphorus concentrations (Figure V-16). The following sections trace the sequential development of the integrated sediment resuspension model for Lake Okeechobee and Lake Apopka sediments. As a final phase of the discussion, sediment resuspension rates and net nutrient release are calculated for several different wind events.

Calculation of Wind-Induced Stress at the Sediment-Water Interface

Surface waves produce an oscillatory motion in the water column that may extend to the bottom in shallow lakes to produce an oscillating horizontal motion. The maximum horizontal velocity at the edge of the bottom boundary layer generated by this periodic motion can be approximated from linear (Airy) wave theory by

$$u_m = \frac{\pi H_s}{T_s \sinh(2\pi d/L_d)} \quad (V-20)$$

where u_m = the maximum horizontal velocity;

H_s = the significant wave height;

T_s = the significant wave period;

d = the local depth; and

L_d = the wavelength for depth, d .

The wavelength L_d may be solved iteratively from

$$L_d = L \tanh\left(\frac{2\pi d}{L_d}\right) \quad (V-21)$$

with

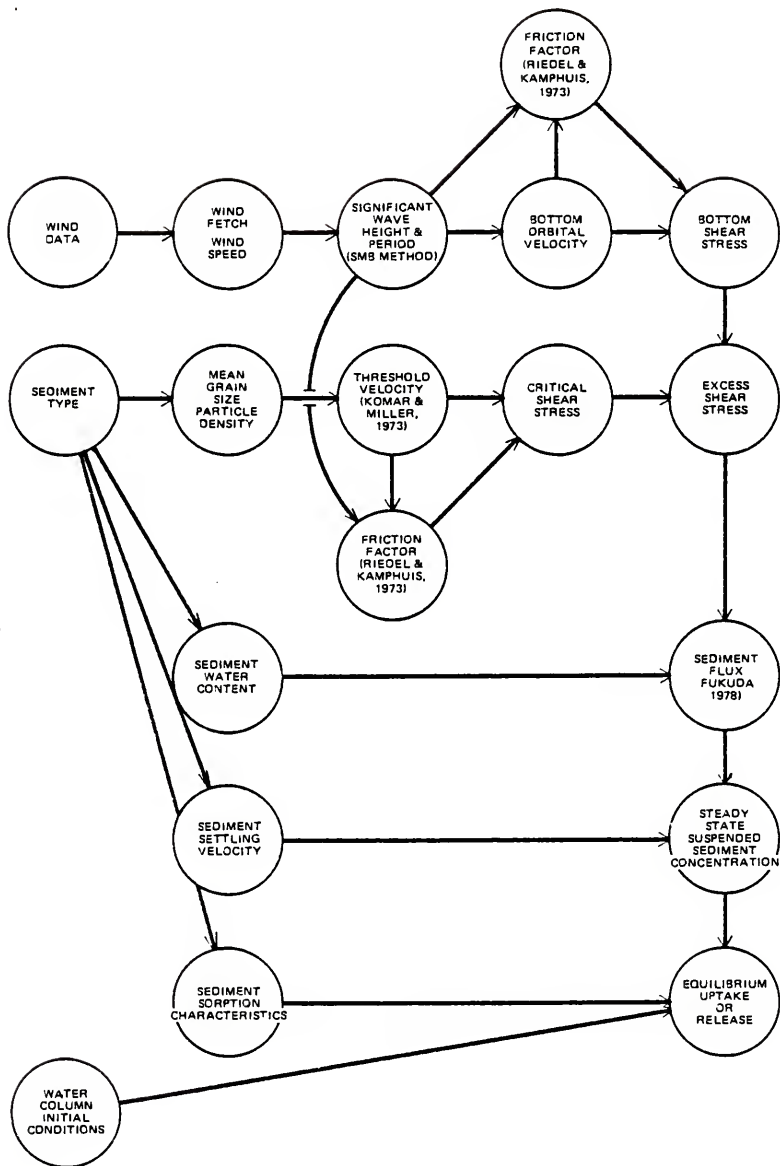


Figure V-16. Schematic Diagram of Sequential Application of the Integrated Sediment Dispersion-Nutrient Release Model.

$$L = \frac{g T_s^2}{2\pi} \quad (V-22)$$

where L = the wavelength in deep water, and
 g = gravitational acceleration.

In the absence of empirical determinations, the significant wave height, H_s , and significant wave period, T_s , at a particular location may be estimated by the Sverdrup-Munk-Bretschneider (SMB) wave hindcasting method (U.S. Army Coastal Engineering Research Center 1977) for shallow water. Input parameters to the model include wind speed and duration, fetch length, and average depth over the fetch. Sheng and Lick (1979) recently compared the predicted results of this and several other hindcasting models to measured wave data from Lake Erie and found the SMB shallow water model to be superior to the other models.

The bottom shear stress generated by the periodic motion of the waves can be expressed as

$$\tau_o = 1/2 \rho f_w u_m^2 \quad (V-23)$$

where ρ = the density of the fluid medium, and
 f_w = the dimensionless wave friction factor.

Riedel and Kamphuis (1973) have shown that f_w is a function of the wave Reynolds number, R_e , and bottom roughness. Similarly Jonsson (1967) developed the following expression for f_w for laminar flow:

$$f_w = 2 \left[\frac{u_m (0.5 d_o)}{\nu} \right]^{-1/2} \quad (V-24)$$

where d_o = the orbital amplitude, and
 ν = the kinematic viscosity of water.

Since the wave Reynolds number can be expressed as

$$R_e = \frac{u_m d_o}{2\nu} \quad (V-25)$$

Equation V-24 reduces to (Madsen and Grant 1975)

$$f_w = 2 (R_e)^{-1/2} \quad (V-26)$$

For fully developed turbulent flow, f_w is independent of R_e (Riedel and Kamphuis 1973; Sheng and Lick 1979). The graphical method of Riedel and Kamphuis (1973) was used in formulating the present model to evaluate f_w as a function of hydrodynamic conditions.

Determination of Critical Shear Stress

Sediment motion in response to a shear stress at the sediment-water interface is not initiated until the stress reaches a critical threshold level. Development of threshold scour criteria for unidirectional flow conditions, which has been of interest for a considerable time, has focused on the use of nondimensional Shields diagrams. The scour criterion established by Shields (1936) expresses the relative (dimensionless) threshold stress, θ_t , as a function of the particle or shear Reynolds number, viz.

$$\theta_t = fct \left(\frac{u_* D}{\nu} \right) \quad (V-27)$$

where

$$\theta_t = \frac{\tau_c}{(\rho_s - \rho)g D} \quad (V-28)$$

where D = the particle diameter, and
 u_* = the critical shear velocity.

The relationship between θ_t and the particle Reynolds number has been determined empirically and is presented in Figure V-17. The Shields curve closely resembles Hjulstrom's (1935) empirical model for particle erosion and deposition in riverine systems as a function of average flow, \bar{u} , and particle size (Figure V-18), and has been verified experimentally for a variety of inorganic sediments (cf. Graf 1971). Furthermore, recent studies conducted by Fisher et al. (1979) demonstrated that organic detrital sediments also conform to the Shields relationship for the initiation of motion.

Comparable studies of the threshold criteria for sediments under wave-induced oscillatory flow are rather limited. Komar and Miller (1973) contended that application of the Shields criterion to define incipient motion of sediment under oscillatory flow can lead to considerable error. Using experimental data of Bagnold (1946), these authors demonstrated substantial scatter for a plot of a modified Shields threshold criterion, θ'_t , versus sediment grain diameter. The threshold parameter θ'_t was defined by the following dimensionless expression:

$$\theta'_t = \frac{\rho u_m^2}{(\rho_s - \rho)g D} \quad (V-29)$$

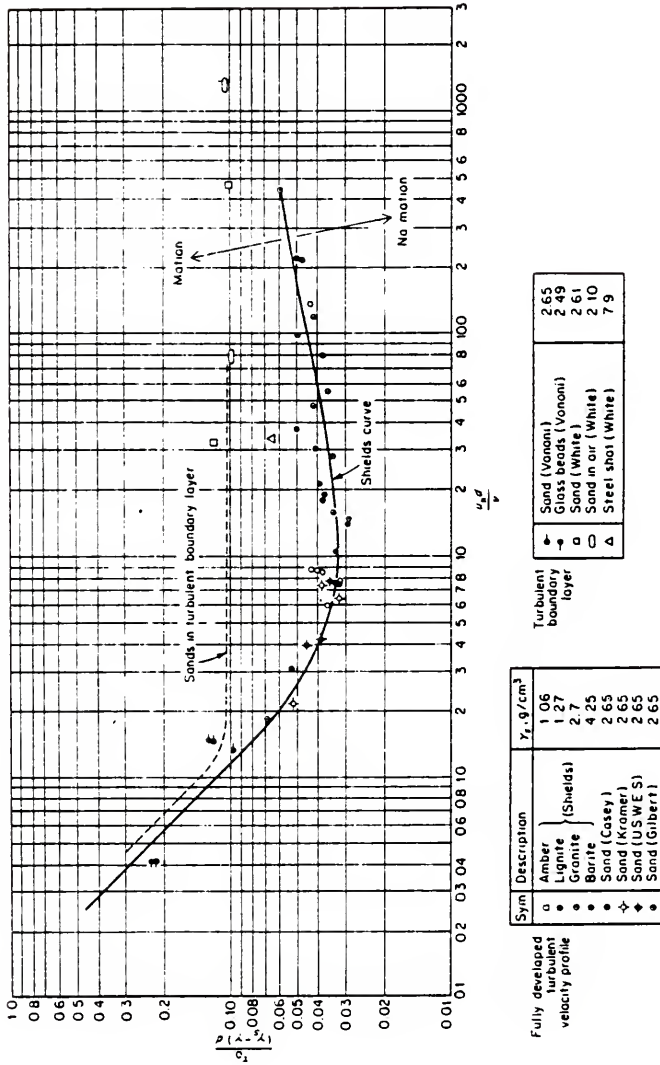


Figure V-17. Shields' Diagram Depicting Dimensionless Critical Shear Stress as a Function of Shear Reynolds Number.

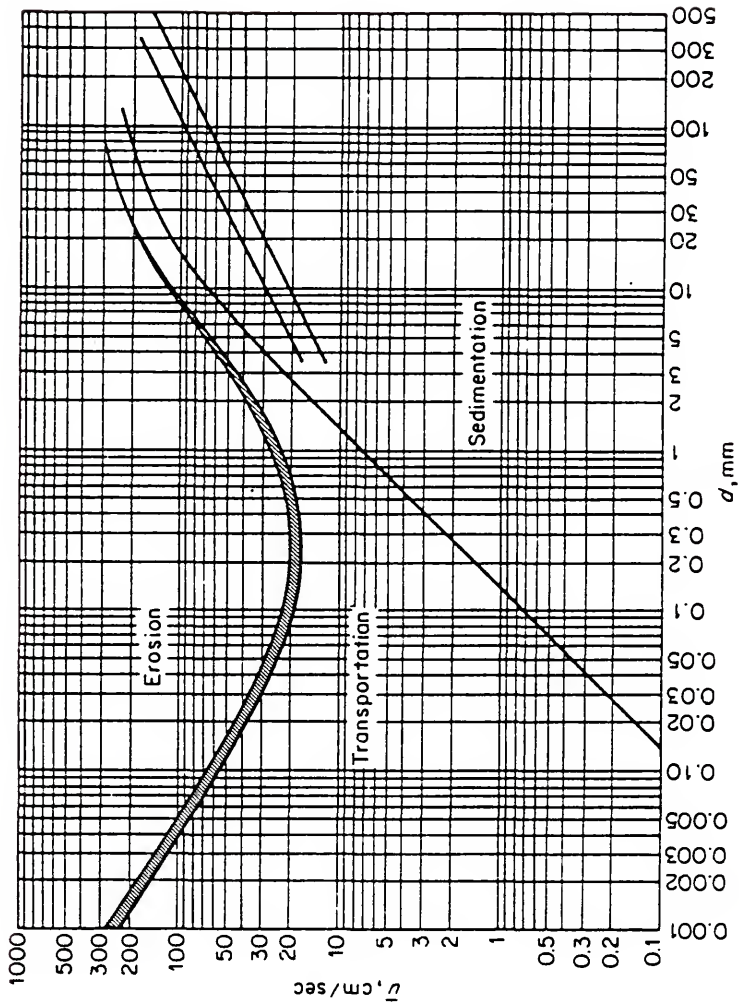


Figure V-18. Erosion-Deposition Criteria for Uniform Particles. From Hjulsrom (1935).

Variability was shown to be related to the wave period, T ; i.e. for a particular sediment grain, transport is initiated at a lower orbital velocity for waves of short period than for waves of long period. This relationship, which has been verified for fine- and medium-sized sediments by Hammond and Collins (1979), can be anticipated from simple wave mechanics which define the orbital velocity as an inverse function of T :

$$u_m = \frac{\pi d_o}{T} \quad (V-30)$$

For sediment particles less than 500 μm in diameter, Komar and Miller (1975) concluded that the threshold point is best related by the following empirical equation:

$$\theta'_t = 0.21 \left(\frac{d_o}{D} \right)^{1/2} \quad (V-31)$$

A similar relationship has been developed by Sternberg and Larsen (1975) for unconsolidated silt-sized sediment:

$$\frac{\rho u_{1/10}^2}{(\rho_s - \rho)g D} = 0.13 \left(\frac{d_o}{D} \right)^{1/2} \quad (V-32)$$

where $u_{1/10}$ = the higher 10 percent of the bottom orbital velocities.

Madsen and Grant (1975) argued that the scatter of Bagnold's (1946) data observed by Komar and Miller (1973) does not necessarily imply the failure of the Shields criterion to define threshold conditions under oscillatory flow. An important difference between Komar and Miller's

θ'_c and the Shields' criterion (θ_c) is found in the numerator of the two expressions: θ_c is a linear function of the critical stress, τ_c (Equation V-28), while θ'_c is a function of fluid density and orbital velocity squared (Equation V-29). For boundary layer flows, applied stress at the bottom is proportional to the square of the near bottom orbital velocity:

$$\tau_o = 1/2 f_w \rho u_m^2 \quad (V-23)$$

Thus, the difference between θ_c and θ'_c is simply the exclusion of the wave friction factor in θ'_c (Komar and Miller 1975; Madsen and Grant 1975). Solution of Equation V-30 for d_o and substitution of the result into Equation V-24 shows that f_w is inversely related to the square root of the wave period (T). This explains the finding of Komar and Miller that θ'_c varies as a function of T for any given sediment. Correspondingly, Madsen and Grant (1975) obtained good agreement between Bagnold's (1946) threshold data and the Shields criterion using the wave friction diagram of Jonsson (1967) to determine f_w . As a result, the authors concluded that the Shields function is quite adequate as a general criterion for the threshold of sediment movement subjected to oscillatory flow. Komar and Miller (1975) independently arrived at the same conclusion.

Calculation of Sediment Resuspension Rates

Several models have been developed to describe sediment resuspension rates as a function of bottom orbital velocities or shear forces. The following empirical expression was developed by Lam and Jaquet (1976) for Lake Erie sediments:

$$J = K_r \left(\frac{\rho_s}{\rho_s - \rho} \right) AU \quad (V-33)$$

where J = the upward (areal) flux of resuspended sediment,

K_r = a dimensionless proportionality constant,

$A = u_a/u_{cr}$ with u_a being a reference velocity equal to 1 cm/s
and u_{cr} is the critical (orbital) velocity, and

$U = u_m - u_{cr}$.

Settling velocity and the regeneration coefficient (K_r) were selected heuristically with J equal to 0.25 m/d and K_r equal to 6.4×10^{-14} .

The structure of this model is quite similar to the expression for bedload transport developed by Sternberg (1972).

Resuspension of western Lake Erie sediments was studied by Sheng and Lick (1979) using an annular flume. From the results of their study, Sheng and Lick developed an empirical physical resuspension model that relates the erosion rate as a two-region linear function of the bottom shear stress:

$$J = c_1 (\tau_o - 0.5) \quad \tau_o \leq 2 \text{ dynes/cm}^2 \quad (V-34)$$

$$J = c_2 (\tau_o - 1.515) \quad \tau_o > 2 \text{ dynes/cm}^2 \quad (V-35)$$

where $c_1 = 1.33 \times 10^{-6}$ s/cm,

$c_2 = 4.12 \times 10^{-6}$ s/cm,

τ_o = dynes/cm² (g/cm/s), and

J = the sediment flux in g/cm²/s.

More extensive studies were conducted by Fukuda (1978) who studied both critical shear stress and entrainment rates for several different substrate types. Fukuda (1978) demonstrated that the rate of

entrainment was dependent not only on the applied stress, but on the water content of the sediment as well; i.e., the rate of entrainment increased both with increasing water content and applied stress. Using sets of data for which τ_c , τ_o , percent water (W), and entrainment rate determinations are available, Fukuda's (1978) results for the central and western basins of Lake Erie can be fit through regression analysis to a multiple linear model:

$$J = -1.30 \times 10^{-5} + 1.66 \times 10^{-6}(\Delta\tau) + 1.87 \times 10^{-7}(W) \quad (V-36)$$

This model is similar in nature to the empirical model developed by Sheng and Lick (1979), but incorporates sedimentary water content to describe the effect of compaction on resuspension rates (Migniot 1968). The effects of sediment grain size and density are implicitly included in the term $\Delta\tau$.

Sediment Dispersion Model

The distribution of sediment particles in suspension due to turbulence is described by the equation for conservation of mass (Graf 1971; Sheng and Lick 1979). In three dimensions, the mass transport equation for the concentration of suspended sediment is

$$\begin{aligned} \frac{\partial M}{\partial t} + \frac{\partial (uM)}{\partial x} + \frac{\partial (vM)}{\partial y} + \frac{\partial [(w + w_s) M]}{\partial z} = \\ \frac{\partial}{\partial x} (D_h \frac{\partial M}{\partial x}) + \frac{\partial}{\partial y} (D_h \frac{\partial M}{\partial y}) + \frac{\partial}{\partial z} (D_v \frac{\partial M}{\partial z}) + S \end{aligned} \quad (V-37)$$

where M = the concentration of sediment particles;
 x and y = the horizontal coordinates;

- z = the vertical coordinate (positive upwards);
 t = time;
 u and v = the velocities in the x and y directions, respectively;
 w = the velocity of sediment (fluid) particles in the z direction;
 w_s = the settling velocity of sediment particles relative to the fluid;
 D_h and D_v = the horizontal and vertical eddy diffusivities, respectively; and
 S = a source term.

The left-hand portion of Equation V-37 represents unsteady and convective components, while the right-hand side represents the turbulent diffusion of suspended sediment and the presence of sources or sinks in the water column.

Of primary interest in this analysis is the vertical distribution of suspended sediment under either steady-state or nonsteady-state condition. Assuming that the horizontal concentration gradients $\partial M / \partial x$ and $\partial M / \partial y$ are zero reduces Equation V-37 to a one-dimensional problem. Furthermore, the source term, S , for sediment generation from within the water column (e.g., derived from algal production and decay) can be assumed to be negligible within the timeframe of interest. Under conditions of oscillatory flow, w has both positive and negative components equating to a net velocity of zero. Finally, the vertical eddy diffusivity, D_v , is assumed to be constant throughout the water column. Under these conditions, Equation V-37 reduces to

$$\frac{\partial M}{\partial t} = D_v \frac{\partial^2 M}{\partial z^2} - w_s \frac{\partial M}{\partial z} \quad (V-38)$$

Several boundary conditions must be imposed if Equation V-38 is to be solvable. At the water surface ($z = h$), mass balance considerations preclude the net vertical flux of sediment particles across the interface, i.e., the turbulent flux of material must balance the convective flux due to settling (Sheng and Lick 1979):

$$D_v \frac{\partial M}{\partial z} - w_s M = 0 \quad (V-39)$$

A second boundary condition can be written at the sediment-water interface ($z = 0$) as follows. Under conditions when sediment entrainment occurs, the net vertical flux of sediment due to settling and turbulent diffusion is balanced by the net erosion rate:

$$D_v \frac{\partial M}{\partial z} - w_s M = \beta M - J \quad (V-40)$$

where β = a proportionality constant with units of velocity; and
 J = the resuspension rate of bottom sediments due to shear stresses generated by waves and currents, as defined in the previous section (Fukuda 1978; Sheng and Lick 1979).

Fukuda (1978) refers to β as the reflectivity parameter; β is inversely related to the fraction of sediment particles reaching the sediment-water interface that are reflected from the interface, and it can range from zero to infinity. As β approaches infinity, an increasing fraction of particles striking the interface are deposited.

A simplified solution for the time-dependent average suspended sediment concentration in the water column can be formulated by integrating both sides of Equation V-38 with respect to z :

$$\int_0^h \frac{\partial}{\partial t} M dz = \int_0^h D_v \frac{\partial^2 M}{\partial z^2} dz - \int_0^h w_s \frac{\partial M}{\partial z} dz \quad (V-41)$$

which may be rewritten as

$$\frac{\partial}{\partial t} \int_0^h M dz = D_v \left. \frac{\partial M}{\partial z} \right|_0^h - w_s M \left|_0^h \right. \quad (V-42)$$

The average concentration, \bar{M} , in the water column at a particular time may be defined as

$$\bar{M} = \frac{1}{h} \int_0^h M dz \quad (V-43)$$

Substituting $\bar{M}(t)$ in Equation V-42 gives

$$h \frac{\partial \bar{M}}{\partial t} = D_v \left. \frac{\partial M}{\partial z} \right|_0^h - w_s M \left|_0^h \right. \quad (V-44)$$

The boundary condition at $z = h$ requires that

$$D_v \frac{\partial M}{\partial z} = w_s M \quad (V-39)$$

while at the sediment-water interface ($z = 0$)

$$D_v \frac{\partial M}{\partial z} = (\beta + w_s) M - J \quad (V-45)$$

Application of the boundary conditions to Equation V-44 yields

$$h \frac{\partial \bar{M}}{\partial t} = J - \beta M_0 \quad (V-46)$$

In other words, the change in average concentration in the water column at particular time t is simply the difference between the mass erosion rate and the net output at the sediment-water interface corrected for the volume defined by h . During steady-state conditions, the concentration at any location within the water column may be derived from Equation V-38 to give

$$M = M_0 e^{-w_s z / D_v} \quad (V-47)$$

where M_0 = concentration at the sediment-water interface ($z = 0$).

Integrating with respect to z gives the average steady-state concentration as a function of M_0

$$\frac{1}{h} \int_0^h M dz = \frac{1}{h} M_0 \int_0^h e^{-w_s z / D_v} dz \quad (V-48)$$

Equation V-48 can be simplified to

$$M_0 = \left[\frac{h w_s}{1 - e^{-w_s h / D_v}} \right] \bar{M} \quad (V-49)$$

Substituting for M_0 in Equation V-46 gives a first order differential equation for \bar{M} as a function of t .

$$\frac{d\bar{M}}{dt} = \epsilon - \psi \bar{M} \quad (V-50)$$

where $\epsilon = J/h$, and

$$\psi = \beta w_s \frac{1}{D_v (1 - e^{-h w_s / D_v})}$$

The time dependent solution for \bar{M} is thus

$$\bar{M}_t = \frac{\epsilon}{\psi} (1 - e^{-\psi t}) \quad (V-51)$$

It is important to realize that Equation V-51 represents a simplified solution and is strictly valid only during steady-state conditions. Under transient or unsteady-state conditions, the concentration profile of suspended sediment deviates from the exponential relationship given by Equation V-47. This error increases as the timeframe of interest becomes increasingly smaller, i.e., as $t \rightarrow 0$. In other words, if the time scale t is such that

$$\frac{D_v t}{h^2} \gg 1 \quad (V-52)$$

and

$$\frac{w_s t}{h} \gg 1 \quad (V-53)$$

the error is negligible.

Under conditions generally found in Lake Apopka and Lake Okeechobee, however, the magnitude of this error is relatively small for timeframes of the order of 24 hours.

Application of the Integrated Model to Lake Apopka and Lake Okeechobee

The contribution of sediment resuspension to nutrient release in Lake Apopka and Lake Okeechobee can be evaluated by applying the integrated sediment dispersion-nutrient release model developed in the previous sections for a set of specified conditions. Sequentially this process (Figure V-16) may be summarized as follows. From wind velocity and direction data, the shear stress at the sediment-water interface can be calculated for a particular locus as a function of both fetch and depth of the water column. The critical shear stress required to initiate sediment resuspension is calculated using the method of Komar and Miller (1973) to determine the threshold velocity as a function of sediment grain size and density (Equations V-29 and V-31), while the graphical method of Riedel and Kamphuis (1973) is used to determine the wave friction factor, f_w , as a function of the predicted wave characteristics. The resulting excess shear stress coupled with the water content of the sediment defines the rate of sediment erosion or upward flux, J (Equation V-36).

The time-dependent average suspended sediment concentration, \bar{M} , is then approximated using Equation V-51. The vertical eddy diffusivity may be calculated from the following relationship between D_v and the wind stress, τ^w (Sheng and Lick 1979):

$$D_v = 9.01 + 8.77|\tau^w| \quad (V-54)$$

where τ^w is given in dyne/cm^2 and D_v is expressed in cm^2/s .

The wind stress τ^w is related to the wind velocity by the quadratic stress law:

$$\tau^w = c_d \rho_a |v|v \quad (V-55)$$

where ρ_a = the air density, and
 c_d = the drag coefficient.

The value of c_d is rather variable; Csanady (1978), for example, indicates that c_d typically assumed a value of 1.6×10^{-3} while Halfon and Lam (1978) reported an average value of 2.4×10^{-3} for the Great Lakes. For the purposes of this model, a value of 1.6×10^{-3} was assumed for c_d . Calculated suspended sediment concentrations are then input to the nutrient release submodel (Equation V-11) to determine the final phosphorus concentration in the water column.

Sediment resuspension was calculated for different locations in Lake Apopka and Lake Okeechobee for which corresponding sorption isotherm data were available for a series of several different wind events. Resuspension and phosphorus release also were modeled at Station A8 under the assumption that sorption characteristics of these sediments are similar to Station A5 sediment. Three different wind velocity events were considered: 6.7 m/s (15 mph), 8.9 m/s (20 mph), and 11.2 m/s (25 mph). Wind intensity was assumed to be constant over a period of 24 hours. Winds were considered to originate from the north for Lake Apopka, corresponding to the prevailing direction generated by sustained frontal activity during the winter months (Fernald 1981). Winds in southern peninsular Florida are typically from the east

(Fernald 1981); consequently, an easterly wind was considered for Lake Okeechobee in this analysis.

The counteracting influence of gravitational settling on resuspension was calculated using settling velocities of 0.050 and 0.047 cm/s for Lakes Apopka and Okeechobee, respectively; these values were determined from settling tube experiments for Station A5 and 014 sediments. The value of the reflectivity parameter, β , was assumed to be 0.008 cm/s and corresponds to the value reported by Sheng and Lick (1979) for a series of different sediment types and experimental conditions.

Net release or uptake of phosphorus was calculated from the predicted average suspended sediment concentration at t equals 24 hours. Initial water column SRP concentrations imposed on the model correspond to average values reported in the literature; for Lake Okeechobee a value of 45 ug P/L was used, which corresponds to the average concentration observed in 1979 (Federico et al. 1981), while Brezonik et al. (1981) reported an average SRP concentration in Lake Apopka of 50 ug P/L for the period 1977 through 1980.

Predicted suspended sediment and equilibrium phosphorus concentrations are presented in Tables V-8 through V-10. In Lake Okeechobee, sufficient wave energy to initiate sediment resuspension occurred at Stations 010 and 013 during the lowest velocity wind event modeled (Table V-8). Under these conditions an average suspended sediment concentration of 0.381 g/L is predicted at Station 010; this equates to a net release of only 2.8 ug P/L and a final phosphorus concentration of 48 ug P/L. Although the effective fetch at Station 013 is nearly a

Table V-8. Summary of Predicted Wave Statistics, Sediment Resuspension Rates, and Final Concentration of SRP at Selected Stations in Lake Okeechobee and Lake Apopka Assuming an Initial Concentration of 45 and 50 ug P/L, Respectively, in the Overlying Water. Wind Velocity is 6.7 m/s and Originates from the East for Lake Okeechobee and from the North for Lake Apopka.

Parameter	Station						
	07	010	011	013	014	A5	A8
H_s (cm)	27	33	38	41	11	24	27
T_s (s)	2.0	2.2	2.3	2.5	1.2	1.8	2.0
L_d (cm)	622	746	806	671	218	515	611
d (cm)	340	240	340	90	180	170	170
u_m (cm/s)	2.77	12.50	7.46	54.0	0.33	10.26	15.00
$u_{m(crit)}$ (cm/s)	5.42	11.5	11.1	13.6	5.77	5.49	5.70
τ_o (dyne/cm ²)	0.52	2.13	1.27	7.72	0.09	1.94	2.66
τ (dyne/cm ²)	1.00	1.97	1.88	2.18	1.39	1.05	1.04
J (g/cm ² -s) $\times 10^6$	--	4.30	--	1.21	--	6.47	7.82
M (g/L)	--	0.381	--	0.133	--	0.628	0.759
$C_{equilibrium}$ (ug P/L)	45	48	45	47	45	81	85

Table V-9. Summary of Predicted Wave Statistics, Sediment Resuspension Rates, and Final Concentration of SRP at Selected Stations in Lake Okeechobee and Lake Apopka Assuming an Initial Concentration of 45 and 50 ug P/L, Respectively, in the Overlying Water. Wind Velocity is 8.9 m/s and Originates from the East for Lake Okeechobee and from the North for Lake Apopka.

Parameter	Station						
	07	010	011	013	014	A5	A8
H_s (cm)	35	41	49	51	15	30	34
T_s (s)	2.3	2.5	2.7	2.9	1.4	2.1	2.3
L_d (cm)	800	928	1,110	785	285	563	641
d (cm)	340	240	340	90	180	170	170
u_m (cm/s)	6.69	21.1	17.0	71.8	1.31	13.9	17.9
$u_{m(crit)}$ (cm/s)	5.66	12.0	11.8	14.2	6.03	5.73	5.95
τ_o (dyne/cm ²)	1.15	3.23	2.60	11.7	0.31	2.43	3.00
τ (dyne/cm ²)	0.97	1.92	1.81	2.12	1.35	1.03	1.01
J (g/cm ² -s) $\times 10^6$	2.84	6.20	3.69	7.92	--	7.33	8.42
\bar{M} (g/L)	0.238	0.591	0.309	0.901	--	0.755	0.867
$C_{equilibrium}$ (ug P/L)	53	49	48	48	45	86	90

Table V-10. Summary of Predicted Wave Statistics, Sediment Resuspension Rates, and Final Concentration of SRP at Selected Stations in Lake Okeechobee and Lake Apopka Assuming an Initial Concentration of 45 and 50 ug P/L, Respectively, in the Overlying Water. Wind Velocity is 11.2 m/s and Originates from the East for Lake Okeechobee and from the North for Lake Apopka.

Parameter	Station						
	07	010	011	013	014	A5	A8
H_s (cm)	41	49	59	60	19	36	39
T_s (s)	2.5	2.8	3.0	3.1	1.5	2.3	2.5
L_d (cm)	959	1,080	1,310	878	351	641	721
d (cm)	340	240	340	90	180	170	170
u_m (cm/s)	11.3	28.9	24.9	86.8	3.13	19.2	23.2
$u_{m(crit)}$ (cm/s)	5.85	12.4	12.2	14.7	6.25	5.92	6.13
τ_o (dyne/cm ²)	1.82	3.97	3.36	15.4	0.68	3.17	3.49
τ (dyne/cm ²)	0.96	1.88	1.78	2.13	1.33	1.01	1.00
J (g/cm ² -s) $\times 10^6$	3.98	7.50	5.00	14.1	--	8.58	9.26
\bar{M} (g/L)	0.357	0.755	0.448	1.642	--	0.924	0.997
$C_{equilibrium}$ (ug P/L)	57	50	50	48	45	93	96

factor of two larger, an average suspended sediment concentration of only 0.133 g/L is predicted. Decreased resuspension relative to Station 010 is due to the sandy nature of sediments at Station 013 and their correspondingly low water content (26.7 percent). Concentrations of SRP in the water column at Station 013 are predicted to increase slightly to 47 ug P/L.

When the wind velocity is increased to 8.9 m/s, sediment resuspension is predicted at all stations in Lake Okeechobee except Station 014 (South Bay). The protected features of South Bay (Figure II-1) limit the effective fetch at Station 014 to approximately 0.5 km and generally precludes sediment resuspension by easterly winds. Highest suspended sediment concentrations are predicted at Station 013, which is characterized by the largest effective fetch of the stations modeled. Although a vertically averaged sediment concentration of 0.901 g/L is predicted at Station 013, only 0.6 mm of the sediment surface is eroded, because of the high bulk density (1.84 g/cm^3) of the sediment. Final SRP concentrations at Stations 010, 011, and 013 show little predicted changes over initial conditions. The greatest releases in Lake Okeechobee (8 ug P/L) occur with Station 07 sediments, which are relatively enriched with labile phosphorus (Table V-2). The net increase in SRP levels at Station 07 is predicted to be 8 ug/L.

Increasing the wind velocity to 11.2 m/s generally has little further influence on predicted in situ SRP concentrations, although the mass flux of sediment to the water column is enhanced substantially (Table V-10). Excluding Station 07, predicted SRP concentrations are elevated by only 5 ug P/L, yielding a final SRP concentration of

50 ug P/L. Net entrainment of the sediment surface ranges from 1 mm at Station 013 to nearly 2 cm at Station 010.

Although the effective fetch of Lake Apopka is generally much less than that of Lake Okeechobee, wind-induced sediment resuspension has a much more pronounced influence on its nutrient regime. Ease of resuspension reflects both the bouyant nature of flocculent, organic sediments and the shallowness of the lake basin. Even under relatively mild conditions, sediment resuspension is substantial in mid-Lake Apopka, resulting in significant release of SRP. For example, wind velocities of 6.7 m/s are predicted to scour 28 mm of the sediment surface at Station A5, resulting in a net release of 31 ug P/L (Table V-8). Desorption from suspended sediments accounts for 18 ug P/L of the predicted change in concentration, and entrained interstitial water accounts for the remaining fraction.

For the same wind velocity conditions, sediment entrainment is only slightly higher at Station A8. The resulting increase in SRP concentration is only 4 ug P/L in excess of the release predicted at Station A5. Because of the high water content of Lake Apopka sediments, sediment resuspension rates are relatively high once the τ_c has been exceeded. Equation V-36 predicts an initial flux of 5.0×10^{-6} g/cm²-s once bed failure occurs and may represent a weakness in the model at low $\Delta\tau$ and high water content. The high rates of resuspension predicted by the model, however, agree qualitatively with empirical observations (see Section IV).

Variability of average suspended sediment concentrations and final SRP concentrations as a function of fetch length are shown in

Figure V-19. For this wind event, resuspension is restricted to regions of the lake having an effective fetch greater than 2.1 km. Once the threshold stress is exceeded, the depth-averaged suspended sediment concentration, \bar{M} , is predicted to increase essentially as a step function from an initial condition of no suspended matter in the water column to 0.460 g/L. Further increases in fetch are predicted to generate relatively small increases in \bar{M} . Correspondingly, final SRP concentrations in the water column are predicted to increase significantly once sediment suspension is induced; beyond the "threshold fetch," however, final SRP concentrations increase slowly with fetch.

The influence of pH on phosphorus release by resuspended sediment is illustrated by Table V-11, which compares predicted final SRP concentrations at Station A5 for several wind velocities as a function of both pH and initial SRP levels in the water column. For example, the net change in SRP at pH 8.3 is predicted to be 36 ug P/L for a sustained wind velocity of 6.7 m/s and an initial SRP concentration of 20 ug P/L in the water column; a shift in pH to 9.30 predicts further release of 18 ug P/L for a total change in SRP of 54 ug P/L. The consequence of pH shift on nutrient release is important because highest pH levels are generally observed in the summer when primary production is maximal; similarly, wind-induced disturbance of the sediments generally is most pronounced during the summer when convective storm activity is greatest.

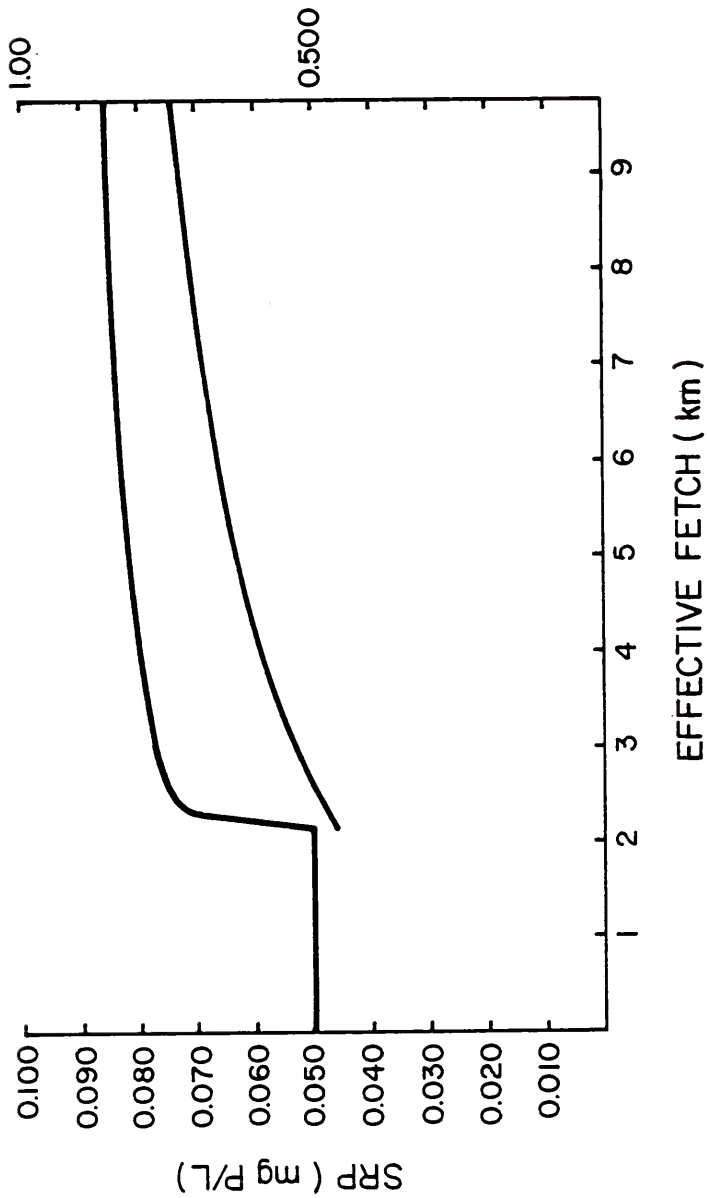
SUSPENDED SEDIMENT, \bar{M} (g/L)

Figure V-19. Predicted Suspended Sediment Concentrations (g/L) (lower curve) and Final SRP Concentrations (mg P/L) (upper curve) in Lake Apopka as a Function of Effective Fetch. Wind Velocity is 6.7 m/s.

Table V-11. Comparison of Predicted Final SRP Concentrations at Station A5 for Various Wind Velocities as a Function of Both pH and Initial SRP Concentration in Water Column.

Initial SRP Concentration (ug P/L)	pH 8.3			pH 9.3		
	6.7 m/s	8.9 m/s	11.2 m/s	6.7 m/s	8.9 m/s	11.2 m/s
20	56	61	68	74	83	94
50	81	86	93	100	108	119

CHAPTER VI DISCUSSION AND SUMMARY

Discussion of Internal Loading

The relative significance of internal loading to the phosphorus dynamics of a lake can be evaluated by constructing a budget quantifying the various phosphorus fluxes through the system. Simplified input-output or mass balance type budget calculations have been used extensively to calculate the net flux of phosphorus to or from sediments (e.g., Bengtsson 1975; Ryding and Forsberg 1977; Cooke et al. 1977). Cooke et al. (1977), for example, used short-term budgets to demonstrate that internal loading was the source of 65 to 105 percent of increases in phosphorus content observed in the eutrophic Twin Lakes (Ohio) following thermal stratification.

Detailed hydrologic and nutrient budgets have been constructed by this author (Brezonik et al. 1978) and Federico et al. (1981) for Lake Apopka and Lake Okeechobee, respectively. The hydrologic and nutrient budgets for both systems were based on the continuity equation:

$$\Delta S = \Sigma I - \Sigma O \quad (\text{VI-1})$$

In other words, the change in storage of a particular constituent in a system (ΔS) is simply the difference between the sum of the inputs (ΣI) and the sum of the outflows (ΣO). Hydraulic income to a lake includes surface inflows from streams, overland runoff, precipitation directly on

the lake's surface, and ground water seepage; hydraulic losses comprise surface outflow, ground water seepage, and evaporation. The hydrologic budget for a lake, therefore, can be expressed in detail by expanding Equation VI-1:

$$\Delta S = (P - E) A + V_i + V_o \pm G \quad (\text{VI-2})$$

where S = change in water storage,
 P = precipitation on lake surface,
 E = evaporation from lake surface,
 A = lake surface area,
 V_i = sum of surface inputs to lake,
 V_o = sum of surface outputs, and
 G = flux of ground water.

Nutrient budgets subsequently were calculated by determining the nutrient flux associated with each particular component of the hydrologic budget.

Hydrologic and nutrient budgets for Lake Apopka were prepared on a monthly basis for the 1977 water year which was prior to the removal of all point source wastewater discharges to the lake in 1978. Federico et al. (1981) presented annual budgets for Lake Okeechobee for the period 1973 through 1979. Table VI-1 summarizes the average hydrologic budgets for Lake Okeechobee and Lake Apopka; while Table VI-2 summarizes the respective phosphorus budgets. The methodology and assumptions inherent in the construction of the monthly budgets for Lake Apopka have been presented by Brezonik et al. (1978) in addition to the monthly results. Federico et al. (1981) provided a more complete discussion of the mass budgets specific to Lake Okeechobee.

Table VI-1. Summary Annual Hydrologic Budget for Lake Okeechobee (1973-1979) and Lake Apopka (1977 Water Year) (all fluxes in $\text{m}^3 \times 10^6$).

	Lake Apopka*	Lake Okeechobee†
<u>Inputs</u>		
Surface	55.6	2,626
Precipitation	131.7	1,666
Seepage	<u>4.0</u>	<u>--</u>
TOTAL	191.3	4,292
<u>Outputs</u>		
Surface	29.2	1,246
Evaporation	163.8	2,541
Seepage	<u>3.6</u>	<u>64</u>
TOTAL	196.6	3,851
Change in Storage	5.3	257
Other Sinks	--	183

* From Brezonik et al. (1978).

† From Federico et al. (1981).

Table VI-2. Summary Annual Phosphorus Budget for Lake Okeechobee (1973-1979) and Lake Apopka (1977 Water Year) (all fluxes in $\text{kg} \times 10^3$).

	Lake Apopka*	Lake Okeechobee†
<u>Inputs</u>		
Surface	33.5	501.6
Precipitation	6.3	100.9
Seepage	<u>1.7</u>	<u>--</u>
TOTAL	41.5	602.5
<u>Outputs</u>		
Surface	5.9	95.2
Seepage	<u>0.8</u>	<u>4.0</u>
TOTAL	6.7	99.2
Change in Storage	--	16.8
Other Sinks	34.8	486.5

* From Brezonik et al. (1978).

† From Federico et al. (1981).

Inspection of external loadings and export rates of phosphorus to and from Lake Apopka and Lake Okeechobee indicates that both systems function as net sinks of phosphorus; i.e., there is a net flux of phosphorus in both lakes is to the sediments (Table VI-2). The magnitude of this flux, which is estimated at 34,800 kg P/y in Lake Apopka and 486,500 kg P/y in Lake Okeechobee, may be expressed as the dimensionless phosphorus retention coefficient, R_p :

$$R_p = 1 - \frac{\Sigma P_{out}}{\Sigma P_{in}} \quad (VI-3)$$

where ΣP_{in} and ΣP_{out} = the total phosphorus mass flux imported to and exported from the system, respectively.

Calculated R_p values for Lake Apopka and Lake Okeechobee are virtually identical (0.84) (Table VI-3).

External loading rates, hydraulic flushing characteristics, and R_p values may be input to simple input/output type modes to compare predicted steady-state concentrations with observed annual average concentrations. The adequacy of this type of model to predict steady-state concentrations correlating with observed values may be taken as an indication of the role of internal loading in controlling phosphorus concentrations in the water column. Baker et al. (1981) recently conducted an extensive review of phosphorus input/output models and applied nutrient loading data for 101 Florida lakes to determine their validity for subtropical lakes. From their analysis these authors concluded that the best predictive equation was a modified version of a model originally derived by Dillon and Rigler (1975):

Table VI-3. Summary of Nutrient Loading Model Input Parameters for Lake Apopka and Lake Okeechobee.

Parameter	Lake Apopka	Lake Okeechobee*
Areal Phosphorus Loading Rate, L_a (g P/m ² -y)	0.334	0.347
Hydraulic Loading Rate† (m/y)	0.48	1.52
Phosphorus Retention Coefficient, R_p (dimensionless)	0.839	0.835
Average Depth, \bar{z} (m)	1.70	2.64
Hydraulic Residence Time, τ_w (year)	6.44	3.47

* Average value for 1973-1979 (Federico et al. 1981).

† Based on surface inflows and seepage (excluding rainfall).

$$TP = 0.748 [L_a(1-R_p)/q_s]^{0.862} \quad (VI-4)$$

where TP = total phosphorus concentration (g/m^3),
 L_a = areal surface loading rate of phosphorus (g/m^2-y), and
 q_s = hydraulic loading rate (m/y).

The two constants were derived through regression analysis to improve the predictability of the original model (enclosed in brackets) for Florida lakes.

The modified Dillon-Rigler model was applied to Lake Apopka and Lake Okeechobee for comparative purposes. This analysis also was extended to a modified Vollenweider (1976) model developed by Baker et al. (1981) for the same data set and to a model recently developed by Chapra (1982). Inclusion of the modified Vollenweider resulted from the work of Federico et al. (1981), who demonstrated good agreement between this model and the average total phosphorus concentration in Lake Okeechobee between 1973 and 1979. In Vollenweider's (1976) model, the apparent deposition or settling velocity of phosphorus to the sediments is assumed to be inversely related to the square root of the hydraulic residence time, τ_w . The modified Vollenweider model has the following form:

$$TP = 0.682 [L_a/q_s(1 + \tau_w)]^{0.934} \quad (VI-5)$$

Chapra's (1982) model, on the other hand, accounts for the resuspension effects by making the apparent settling velocity a function of lake depth:

$$v_p = v_{\max} (1 - e^{-\alpha z}) \quad (\text{VI-6})$$

where v_{\max} = the maximum apparent settling velocity (m/y), and
 α = a parameter to describe the effect of depth on the decay
of v_{\max} .

The resulting steady-state model is given by Chapra (1982) as

$$\text{TP} = \text{TP}_i (1 - f_s) [1 + v_{\max} (1 - e^{-\alpha z}) / q_s]^{-1} \quad (\text{VI-7})$$

where TP_i = total phosphorus concentration of the input, and
 f_s = the fraction of the input that does not affect mid-lake
quality.

Required model parameters including L_a and q_s specific to Lake Apopka and Lake Okeechobee are summarized in Table VI-3; results for predicted and observed phosphorus concentrations are presented in Table VI-4. Using the data of Schaffner and Oglesby (1978) and Oglesby and Schaffner (1978), Chapra (1982) estimated values for v_{\max} and α as 24.5 m/y and 0.075 m/y, respectively. These values were subsequently used in the analysis. The entire phosphorus input to each lake was assumed to influence lake phosphorus concentrations (i.e., $f_s = 0$). Predicted and observed (average) values for Lake Okeechobee agree rather well for all three models and this suggests that external loading processes are controlling the lake's nutrient regime. These results are also consistent with the relationship observed between the temporal distribution of total phosphorus concentrations and annual external loading rates (Figure VI-1). Total phosphorus levels have been increasing steadily 0.049 mg P/L in 1973 to 0.097 mg P/L in 1979

Table VI-4. Application of Total Phosphorus Predictive Models to Lake Apopka and Lake Okeechobee.

	Observed Average Total Phosphorus Concentration (mg P/L)	Modified Vollenweider* (1976)	Modified Dillon & Rigler† (1975)	Chapra** (1982)
Apopka	0.221	0.149	0.113	0.098
Okeechobee	0.063	0.064	0.051	0.059

$$* \text{ TP} = 0.682 [L_a/q_s (1 + \tau_w)]^{0.934} \text{ (Brezonik et al. 1982).}$$

$$\dagger \text{ TP} = 0.748 [L_a (1-R_p)/q_s]^{0.862} \text{ (Baker et al. 1982).}$$

$$** \text{ TP} = \text{TP}_i (1-f_s) [1 + v_{\max} (1-e^{-\alpha z})/q_s]^{-1}.$$

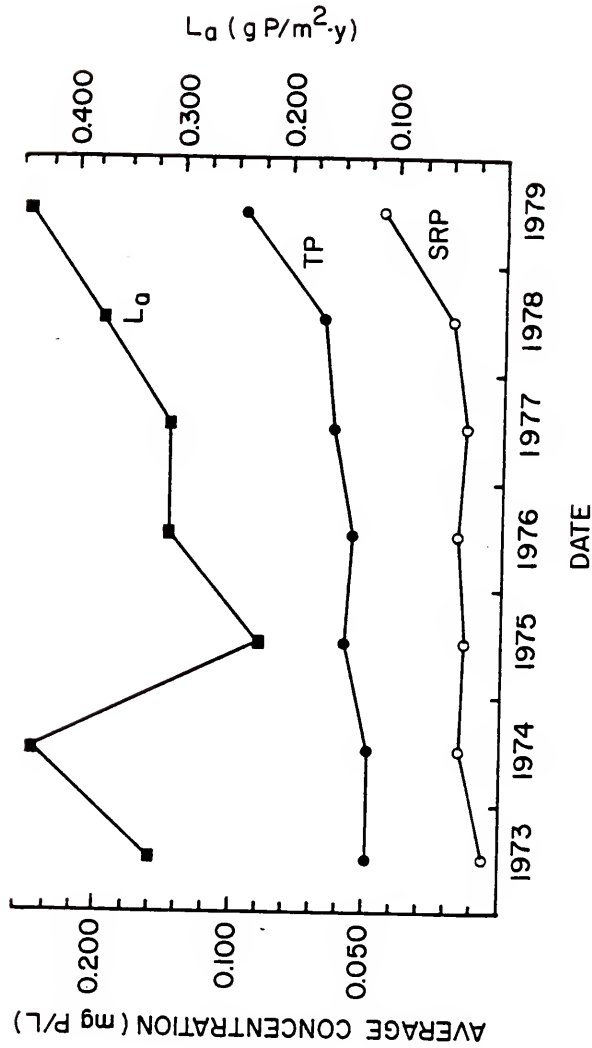


Figure VI-1. Areal Phosphorus Loading Rates, L_a (g P/m²·yr), and Annual Average SRP and Total Phosphorus (TP) Concentrations (mg P/L) in Lake Okeechobee from 1973 through 1979. Data from Federico et al. (1981).

(Federico et al. 1981), and this trend generally corresponds to increases in external loading rates. This general trend is not observed in 1974 and 1975 when L_a increased sharply in 1974 to $0.437 \text{ g/m}^2\text{-y}$ and then fell to $0.227 \text{ g/m}^2\text{-y}$ in 1975; total phosphorus concentrations during the period increased slightly.

Application of the nutrient loading models to Lake Apopka shows poor agreement between the average total phosphorus concentration observed in 1977 and predicted concentrations (Table VI-4). All three models predicted concentrations that are too low; the best approximation was given by the modified Vollenweider model, which predicts a steady-state concentration of 0.149 mg P/L compared with an average concentration of 0.221 mg P/L . This discrepancy implies that internal loading exerts a substantially greater influence than the model accounts for. Further evidence of the relative importance of internal loading to the nutrient dynamics is given by Figure VI-2 which shows the annual average concentration of total phosphorus in Lake Apopka as a function of time. Although nutrient loading data are not available beyond 1977, nutrient loadings to Lake Apopka have undoubtedly decreased with the cessation of all point-source wastewater discharges in 1978.

Despite reduced rates of nutrient import, average total phosphorus concentrations were highest in 1978 and 1979 and probably are attributable to nutrient release from resuspended sediments. Such a mechanism is also supported by the stochastic distribution of mean monthly concentrations in Lake Apopka during the study period. No seasonal trends are evident, and concentrations of both SRP and total phosphorus increase and decrease quite markedly as a result of internal loading and subsequent uptake by algae and settling processes, respectively.

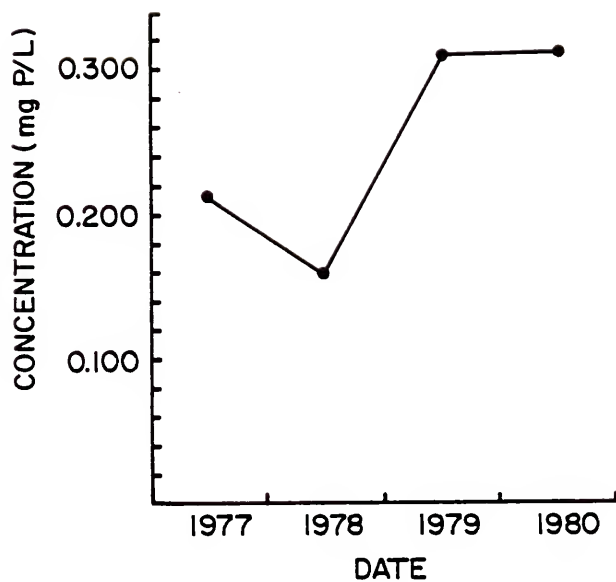
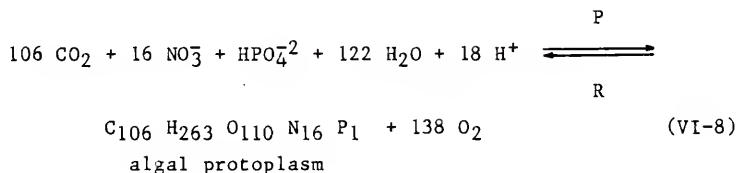


Figure VI-2. Average Annual Total Phosphorus (TP) Concentrations (mg P/L) in Lake Apopka from 1977 through 1980. Data from Brezonik et al. (1981).

An alternative approach to assessing the magnitude of internal loading to the trophic status of a lake is to evaluate the nutritional demands of primary producers and quantify the various sources satisfying that demand. Implicit in this analysis is the recognition that the recycling rate or turnover time of phosphorus in the trophogenic zone may be much more important than the steady-state concentration in limiting primary production. Golterman (1973), for example, suggests phosphorus turnover times of the order of 5 to 10 days.

Algal uptake requirements for phosphorus may be calculated indirectly from the Redfield stoichiometric relationship (Redfield et al. 1963):



For Lake Apopka, with an average primary production rate of $911 \text{ g C/m}^2\text{-y}$ (Brezonik et al. 1978), this relationship implies a phosphorus uptake rate of $22.2 \text{ g P/m}^2\text{-y}$. The lack of primary production data precludes a similar analysis for Lake Okeechobee. Given an average concentration of 0.221 g/m^3 in Lake Apopka during the same period, an average phosphorus turnover time of 6.2 days is calculated. If approximately 10 percent of the total phosphorus mass during each cycle is not recycled but is lost to the sediments a total loss for the system of about $2.2 \text{ g/m}^2\text{-y}$ is calculated. Of the required inputs necessary to balance this deficit, external loading contributes approximately

15 percent (Figure VI-3). Diffusion from the sediments, which was estimated to range between 1.6 to 4.3 g P/m²-d generates an annual flux of 0.6 to 1.6 g P/m². The remaining fraction required to balance the phosphorus uptake flux by primary producers may be accounted for by resuspension (0.3 to 1.3 g P/m²-d). Assuming a net concentration increase of 30 ug P/L or greater characterizes the flux of phosphorus from resuspended sediments during sustained wind events of 6.7 m/s or greater, between 6 and 25 wind events are required annually to generate the flux required by the simplified uptake model. When compared to the annual average number of thunderstorm days in Orlando (74.4) (Davis and Sakamoto 1976), 25 km southeast of Lake Apopka, it is apparent that wind-induced resuspension may assume an even more substantial role in controlling the nutrient dynamics of Lake Apopka.

Summary

The shallow nature and broad fetch characteristic of Lake Apopka (mean depth 1.7 m) and Lake Okeechobee (mean depth 2.8 m) suggest that sediment resuspension and the concomitant release of sorbed phosphorus may be important in the cycling of phosphorus. As a result, a model was developed incorporating physical, chemical, and hydrodynamic components to predict internal loading of phosphorus in shallow lakes. Phosphorus releases are predicted on a single event basis in response to wind-driven turbulent mixing in the water column. The model synthesizes a wave-hindcasting submodel to determine sediment resuspension rates and a phosphorus release submodel derived from Langmuir sorption theory. Langmuir constants used as model inputs were derived from adsorption-desorption isotherms conducted at controlled pH.

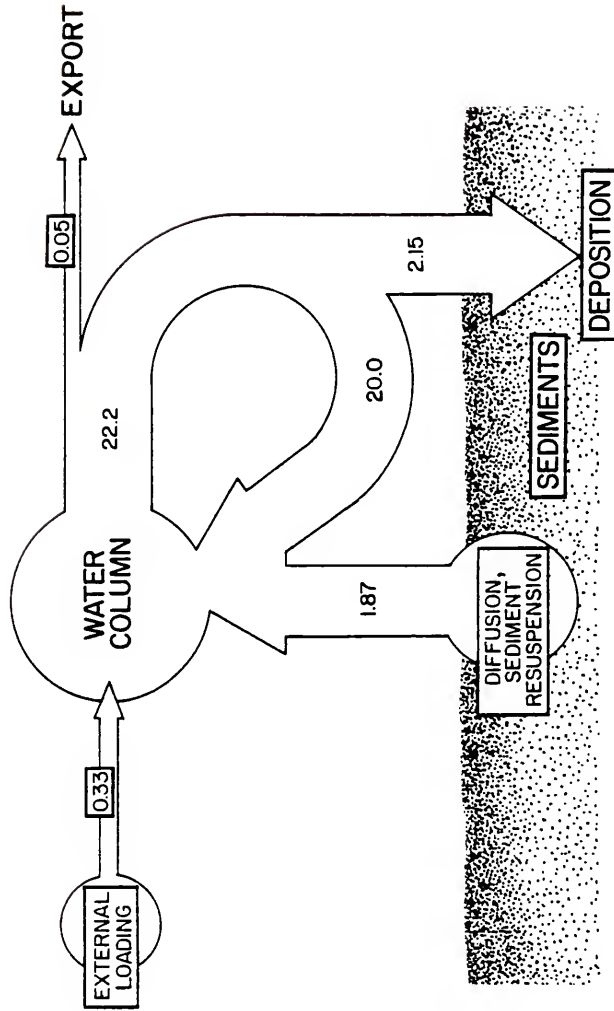


Figure VI-3. Allochthonous Phosphorus Inputs and the Phosphorus Cycle in Lake Apopka. All Fluxes are Given as $\text{g P/m}^2\text{-y}$.

Under ambient conditions in the water column, both Lake Apopka and Lake Okeechobee sediments are predicted to release phosphorus upon resuspension. Model results indicate that a moderate wind event (approximately 8.9 m/s) can more than double mid-lake concentrations of orthophosphorus in Lake Apopka from 20 to 61 ug P/L at pH 8.3. Predicted phosphorus release from Lake Okeechobee sediments under the same wind conditions is substantially lower (approximately 3 to 8 ug P/L). Release is primarily from desorptive processes, although in Lake Apopka entrained pore fluid contributes approximately 30 percent of the net release. Release in both lakes is predicted to be maximal during the summer when high rates of photosynthesis shift lakewater pH upward, thus enhancing the magnitude of desorption. The cumulative effect of cyclonic and convective disturbances during the course of a year results in internal loading in Lake Apopka easily exceeding external loading rates. Sediment resuspension is less significant in Lake Okeechobee, and the nutrient regime appears to be controlled primarily by external loading.

Turbulent mixing and nutrient release studies conducted on fresh and dessicated sediments indicate lake drawdown will effectively stabilize bottom sediments in Lake Apopka and greatly diminish wind-induced sediment resuspension. Upon refill of the lake, however, a large release of phosphorus is predicted. After a stabilization period of several months, overlying water SRP concentrations are expected to return to lower levels.

The integrated nutrient release-sediment resuspension model should be viewed as semi-quantitative. The conjunctive influence of applied

shear stress, critical shear stress, and water content on sediment erosion rates is not adequately described for lacustrine sediments beyond the Lake Erie basin. Ease of resuspension is affected by the amount of elapsed time between periods of disturbance which may confound attempts to accurately quantify sediment resuspension rates in Lake Apopka and Lake Okeechobee. In addition, the sediment resuspension model is sensitive to changes in the reflectivity parameter (β); additional research is required to determine this parameter specific to both lakes. Despite these limitations, results from sorption studies demonstrate that under current conditions in both Lake Apopka and Lake Okeechobee, net release of phosphorus occurs upon sediment resuspension. This mechanism is undoubtedly a major contributing factor accounting for the stochastic nature of phosphorus dynamics in Lake Apopka and Lake Okeechobee.

REFERENCES

- Alishahi, M.R., and R.B. Krone. 1964. Suspension of cohesive sediments by wind-generated waves. Hydraulic Engineering Laboratory, Univ. California, Berkeley. Tech. Rept. HEL-2-9.
- Allan, R.J., J.D.H. Williams, S.R. Joshi, and W.F. Warwick. 1980. Historical changes and relationship to internal loading of sediment phosphorus forms in hypertrophic prairie lakes. *J. Environ. Qual.* 9:199-206.
- Aller, R.C. 1978. Experimental studies of changes produced by deposit feeders on pore water, sediment, and overlying water chemistry. *Am. J. Sci.* 278:1185-1234.
- Aller, R.C. 1980. Quantifying solute distributions in the bioturbated zone of marine sediments by defining an average microenvironment. *Geochim. Cosmochim. Acta* 44:1955-1965.
- American Public Health Association. 1976. Standard methods for the examination of water and wastewater. 14th Ed. American Public Health Association.
- Andersen, J.M. 1974. Nitrogen and phosphorus budgets and the role of sediments in six shallow Danish lakes. *Arch. Hydrobiol.* 74:528-550.
- Armstrong, D.E. 1979. Phosphorus transport across the sediment-water interface, p. 169-175. *In* Lake restoration. Proc. of a national conf., Aug. 22-24, 1978. EPA-440/5-79-001. U.S. Environmental Protection Agency.
- Arulanandan, K., P. Loganathan, and R.B. Krone. 1975. Pore and eroding fluid influences on surface erosion of soil. *J. Geotech. Eng. Div. ASCE* 101:51-66.
- Atkinson, R.J., R.L. Parfitt, and R.St.C. Smart. 1974. Infra-red study of phosphate adsorption on goethite. *J. Chem. Soc. Farad. Trans.* 1:1472-1479.
- Bache, B.W., and E.G. Williams. 1971. A phosphate sorption index for soils. *J. Soil Sci.* 22:289-301.
- Bagnold, R.A. 1946. Motions of waves in shallow water: Interaction between waves and sand bottoms. *Proc. Royal Soc. London* 187 (Series A):1-15.

- Baker, L.A., P.L. Brezonik, and C.R. Kratzer. 1981. Nutrient loading--trophic state relationships in Florida lakes. Water Resource Research Center Publication 56. Univ. Florida.
- Banoub, M.W. 1975. Experimental studies on material transactions between mud and water of the Gnadensee (Bodensee). Verh. Internat. Verein. Limnol. 19:1263-1271.
- Barica, J. 1974. Some observations on internal recycling, regeneration, and oscillation of dissolved nitrogen and phosphorus in shallow self-contained lakes. Arch. Hydrobiol. 74:334-360.
- Barr, A.J., J.H. Goodknight, J.P. Sall, and J.T. Halwig. 1976. A user's guide to SAS 76. SAS Institute, Inc.
- Bascom, W. 1964. Waves and beaches. Doubleday.
- Bengtsson, L. 1975. Phosphorus release from a highly eutrophic lake sediment. Verh. Internat. Verein. Limnol. 19:1107-1116.
- Berger, W.H., and G.R. Heath. 1968. Vertical mixing in pelagic sediments. J. Mar. Res. 26:134-143.
- Berner, R.A. 1971. Principles of chemical sedimentology. McGraw-Hill.
- Berner, R.A. 1976. Inclusion of adsorption in the modeling of early diagenesis. Earth Planetary Sci. Letters 29:330-340.
- Berner, R.A. 1980. Early Diagenesis: A theoretical approach. Princeton University Press.
- Born, S.M. 1979. Lake rehabilitation: A status report. Environ. Management 3(2):145-153.
- Brezonik, P.L., E.C. Blancher, V.B. Myers, C.L. Hilty, M.K. Leslie, C.R. Kratzer, G.D. Marbury, B.D. Snyder, T.L. Crisman, and J.J. Messer. 1979. Factors affecting primary production in Lake Okeechobee, Florida. Rept. No. ENV-07-79-01. Dept. of Env. Eng. Sci., Univ. Florida.
- Brezonik, P.L., C.D. Pollman, T.L. Crisman, J.N. Allison, and J.L. Fox. 1978. Limnological studies on Lake Apopka and the Oklawaha chain of lakes. 1: Water quality in 1977. Rept. No. ENV-07-78-01. Dept. of Env. Eng. Sci., Univ. Florida.
- Brezonik, P.L., S.D. Preston, and T.L. Crisman. 1981. Limnological studies on Lake Apopka and the Oklawaha chain of lakes. 4: Water quality in 1980. Rept. No. ENV-07-81-02. Dept. of Env. Eng. Sci., Univ. Florida.
- Brezonik, P.L., and E.E. Shannon. 1971. Trophic state of lakes in north central Florida. Water Resource Research Center Publication-13, Univ. Florida.

- Brooks, H.K. 1974. Lake Okeechobee. In P.J. Gleason (ed.), Environments of south Florida: Present and past. Memoir 2, Miami Geological Society.
- Bush, P.W. 1974. Hydrology of the Oklawaha Lakes area of Florida. U.S. Geol. Survey Map Series No. 69.
- Carritt, D.E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep-Sea Res. 1:224-243.
- Chang, S.C., and M.L. Jackson. 1957. Fractionation of soil phosphorus. J. Soil Sci. 84:133-144.
- Chapra, S.C. 1982. A budget model accounting for the positional availability of phosphorus in lakes. Water Res. 16:205-209.
- Cooke, G.D., M.R. McComas, D.W. Waller, and R.H. Kennedy. 1977. The occurrence of internal phosphorus loading in two small eutrophic lakes in northeastern Ohio. Hydrobiologia 56:129-135.
- Csanady, G.T. 1978. Water circulation and dispersal mechanisms, p. 21-64. In A. Lerman (ed.), Lakes: Chemistry, geology, physics. Springer-Verlag.
- Davis, M.B., and M.S. Ford. 1982. Sediment focusing in Mirror Lake, New Hampshire. Limnol. Oceanogr. 27:137-150.
- Davis, F.E., and M.L. Marshall. 1975. Chemical and biological investigations of Lake Okeechobee, January 1973-June 1974. Interim report. Central and Southern Florida Flood Control Dist. Tech. Publ. No. 75-1.
- Davis, J.M., and C.M. Sakamoto. 1976. An atlas and tables of thunderstorm and hail day probabilities in the southeastern United States. Agricultural Experiment Station Bull. No. 477. Auburn Univ.
- Dean, W.E., and E. Gorham. 1976. Major chemical and mineral components of profundal surface sediments in Minnesota lakes. Limnol. Oceanogr. 21:259-284.
- Digiano, F.A., and P.D. Snow. 1977. Consideration of phosphorus release from sediments in a lake model, p. 318-323. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Dillon, P.J., and F.H. Rigler. 1975. A simple method for predicting the capacity of a lake for development based on lake trophic status. J. Fish. Res. Bd. Can. 31:1518-1531.

- East Central Florida Regional Planning Council. 1973. Upper Oklawaha River Basin water quality management plan. U.S. Environmental Protection Agency.
- Edzwald, J.K. 1977. Phosphorus in aquatic systems: The role of the sediments, p. 183-214. In I.H. Suffett (ed.), Fate of pollutants in the air and water environments, part 1, v. B. Wiley.
- Edzwald, J.D., D.C. Toensing, and M.C.-Y. Leung. 1976. Phosphate adsorption reactions with clay minerals. Environ. Sci. Technol. 10:485-490.
- Ellis, J. 1980. A convenient parameter for tracing leachate from sanitary landfills. Water Res. 14:1283-1287.
- Federico, A.C., K.G. Dickson, C.R. Kratzer, and F.E. Davis. 1981. Lake Okeechobee water quality studies and eutrophication assessment. South Florida Water Management District Tech. Pub. 81-2.
- Fee, E.J. 1979. A relation between lake morphometry and primary productivity and its use in interpreting whole-lake eutrophication experiments. Limnol. Oceanogr. 24:401-416.
- Fernald, E.A. 1981. Atlas of Florida. Florida State Univ. Foundation.
- Fillos, J., and H. Biswas. 1976. Phosphate release and sorption by Lake Mohegan sediments. Jour. Env. Eng. Div., Proc. Am. Soc. Civ. Eng. 102 (EE6):239-248.
- Fisher, J.S., J. Pickral, and W.E. Odum. 1979. Organic detritus particles: Initiation of motion criteria. Limnol. Oceanogr. 24:529-532.
- Fitter, A.H., and C.D. Sutton. 1975. The use of the Freundlich isotherm for soil phosphate sorption data. J. Soil Sci. 26:241-246.
- Fox, J.L., P.L. Brezonik, and M.A. Keirn. 1977. Lake drawdown as a method of improving water quality. U.S. EPA Ecological Research Series. EPA-600/3-77-005.
- Frink, C.R. 1967. Nutrient budget: rational analysis of eutrophication in a Connecticut lake. Environ. Sci. Tech. 1:425-428.
- Frink, C.R. 1969. Chemical and mineralogical characteristics of eutrophic lake sediments. Soil Sci. Soc. Am. Proc. 33:369-372.
- Fukuda, M.K. 1978. The entrainment of cohesive sediments in freshwater. Ph.D. thesis. Case Western Reserve Univ.

- Gahler, A.R. 1969. Sediment-water interchange, p. 243-257. In Proc. eutrophication biostimulation assessment workshop. Univ. California, Berkeley.
- Golterman, H.L. 1973. Natural phosphate sources in relation to phosphate budgets: A contribution to the understanding of eutrophication. Water Res. 7:3-17.
- Golterman, H.L. 1977. Sediments as a source of phosphate for algal growth, p. 286-293. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Graf, W.H. 1971. Hydraulics of sediment transport. McGraw-Hill.
- Green, D.B., T.J. Logan, and N.E. Smeck. 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin in Ohio. J. Environ. Qual. 7:208-212.
- Griffin, R.A., and J.J. Jurinak. 1973. The interaction of phosphate with calcite. Soil Sci. Soc. Am. Proc. 37:847-850.
- Griffin, R.A., and J.J. Jurinak. 1974. Kinetics of the phosphate interaction with calcite. Soil Sci. Soc. Am. Proc. 38:75-79.
- Grobler, D.C., and E. Davies. 1979. The availability of sediment phosphate to algae. Water S.A. 5:114-122.
- Grundmanis, V., and J.W. Murray. 1977. Nitrification and denitrification in marine sediments from Puget Sound. Limnol. Oceanogr. 22:804-813.
- Guy, H.P. 1969. Laboratory theory and methods for sediment analysis. Book 5, Chapt. C1, Techniques of water-resources investigations of the United States Geological Survey. U.S. Geological Survey.
- Hakanson, L. 1977. The influence of wind, fetch, and water depth on the distribution of sediments in Lake Vanern, Sweden. Can. J. Earth Sci. 14:397-412.
- Hakanson, L. 1981. Determination of characteristic values for physical and chemical lake sediment parameters. Water Resour. Res. 17:1625-1640.
- Hammond, T.M., and M.B. Collins. 1979. On the threshold of transport of sand-sized sediment under the combined influence of unidirectional and oscillatory flow. Sedimentology 26:795-812.
- Hargrave, B.T., and G.F. Connolly. 1978. A device to collect supernatant water for measurement of the flux of dissolved compounds across sediment surfaces. Limnol. Oceanogr. 23:1005-1010.

- Harter, R.D., and B.B. Foster. 1976. Computer simulation of phosphorus movement through soils. *Soil Sci. Soc. Am. J.* 40:239-242.
- Hingston, F.J., R.J. Atkinson, A.M. Posner, and J.P. Quirk. 1967. Specific adsorption of anions. *Nature* 215:1459-1461.
- Hingston, F.J., A.M. Posner, and J.P. Quirk. 1974. Anion adsorption by goethite and gibbsite, II. Desorption of anions from hydrous oxide surfaces. *J. Soil Sci.* 25:16-26.
- Hjulstrom, F. 1935. The morphological activity of rivers as illustrated by the River Fyris. *Bull. Geol. Inst. Uppsala* 25:292-492.
- Holdren, G.C., and D.E. Armstrong. 1980. Factors affecting phosphorus release from intact lake sediment cores. *Environ. Sci. Technol.* 14:79-87.
- Holford, I.C.R. 1978. Soil adsorption phenomena and the Langmuir equation. *Soil Sci. Soc. Am. J.* 42:986-987.
- Holford, I.C.R., and G.E.G. Mattingly. 1975. The high- and low-energy phosphate adsorbing surfaces in calcareous soils. *J. Soil Sci.* 26:407-417.
- Holford, I.C.R., and G.E.G. Mattingly. 1976. Phosphate adsorption and plant availability of phosphate. *Plant Soil* 44:219-229.
- Holm, T.R., M.A. Anderson, D.G. Iverson, and R.S. Stanforth. 1979. Heterogeneous interactions of arsenic in aquatic systems, p. 711-736. In E.A. Jenne (ed.), *Chemical modeling in aqueous systems*. ACS Symposium Series No. 93.
- Hope, G.D., and J.K. Syers. 1976. Effects of solution: soil ratio on phosphate sorption by soils. *J. Soil Sci.* 27:301-306.
- Huettl, P.J., R.C. Wendt, and R.B. Corey. 1979. Prediction of algal-available phosphorus in runoff suspensions. *J. Environ. Qual.* 8:130-132.
- Hutchinson, G.E. 1957. *A treatise on limnology, I. Geography, physics, and chemistry*. Wiley.
- Hwang, C.P., T.H. Lackie, and P.M. Huang. 1976. Adsorption of inorganic phosphate by lake sediments. *J. Water Pollut. Control Fed.* 48:2755-2760.
- Imboden, D.M. 1975. Interstitial transport of solutes in non-steady state accumulating and compacting sediments. *Earth Plan. Sci. Lett.* 27:221-228.

- Jaycock, M.J., and G.D. Parfitt. 1981. Chemistry of interfaces. Halsted.
- Jones, B.F., and C.J. Bowser. 1978. The mineralogy and related chemistry of lake sediments, p. 179-235. In A. Lerman (ed.), Lakes: Chemistry, geology, physics. Springer-Verlag.
- Jonsson, I.G. 1967. Wave boundary layers and friction factors, p. 127-148. In Proc. 10th Conf. on Coastal Engr. American Society of Civil Engineers.
- Kamp-Nielsen, L. 1974. Mud-water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting the exchange rates. Arch. Hydrobiol. 73:218-237.
- Kamp-Nielsen, L. 1975. Seasonal variation in sediment-water exchange of nutrient ions in Lake Esrom. Verh. Internat. Verein. Limnol. 19:1057-1065.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.
- Kelts, K., and K.J. Hsu. 1978. Freshwater carbonate sedimentation, p. 295-323. In A. Lerman (ed.), Lakes: Chemistry, geology, and physics. Springer-Verlag.
- Klump, J.V., and C.S. Martens. 1981. Biogeochemical cycling in an organic-rich coastal marine basin, II. Nutrient sediment-water exchange processes. Geochim. Cosmochim. Acta 45:101-121.
- Komar, P.D., and M.C. Miller. 1973. The threshold of sediment movement under oscillatory water waves. J. Sediment. Petrol. 43/4:1101-1110.
- Komar, P.D., and M.C. Miller. 1975. On the comparison between the threshold of sediment motion under waves and unidirectional currents with a discussion of the practical evaluation of the threshold. J. Sediment. Petrol. 45/1:362-367.
- Krezoski, J.R., S.C. Mozley, and J.A. Robbins. 1978. Influence of benthic macroinvertebrates on mixing of profundal sediments in southeastern Lake Huron. Limnol. Oceanogr. 23:1011-1016.
- Krom, M.D., and R.A. Berner. 1980a. Adsorption of phosphate in anoxic marine sediments. Limnol. Oceanogr. 25:797-806.
- Krom, M.D., and R.A. Berner. 1980b. The diffusion coefficients of sulfate, ammonium, and phosphate ions in anoxic marine sediments. Limnol. Oceanogr. 25:327-337.

- Krone, R.B. 1976. Engineering interest in the benthic boundary layer, p. 143-156. In I.N. McCave (ed.), The benthic boundary layer. Plenum.
- Ku, W.C., F.A. Digiano, and T.H. Feng. 1978. Factors affecting phosphate adsorption equilibria in lake sediments. Water Res. 12:1069-1074.
- Kuo, S., and Lotse, E.G. 1974. Kinetics of phosphate adsorption and desorption by lake sediments. Soil Sci. Soc. Am. Proc. 38:50-54.
- Lam, D.C.L., and J.-M. Jaquet. 1976. Computations of physical transport and regeneration of phosphorus in Lake Erie, Fall 1970. J. Fish. Res. Bd. Can. 33:550-563.
- Lam, D.C.L., and E. Halfon. 1978. Model of primary production, including circulation influences, in Lake Superior. Appl. Math. Modeling 2:30-40.
- Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica, and platinum. J. Amer. Chem. Soc. 40:1361-1402.
- Lastein, E. 1976. Recent sedimentations and resuspension of organic matter in eutrophic Lake Esrom, Denmark. Oikos 27:44-49.
- Lee, G.F., W.C. Sonzogni, and R.D. Spear. 1977. Significance of oxic vs. anoxic conditions for Lake Mendota sediment phosphorus release, p. 297-306. In H.L. Golterman (ed.), Interactions between sediments and fresh waters. Junk.
- Lehninger, A.L. 1970. Biochemistry. Worth.
- Lerman, A. 1979. Geochemical processes: Water and sediment environments. Wiley-Interscience.
- Li, W.C., D.E. Armstrong, J.D.H. Williams, R.F. Harris, and J.K. Syers. 1972. Rate and extent of inorganic phosphate exchange in sediments. Soil Sci. Soc. Am. Proc. 36:279-285.
- Li, Y.-H., and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta 38:703-714.
- Lijklema, L. 1977. The role of iron in the exchange of phosphate between water and sediments, p. 313-317. In H.L. Golterman (ed.), Interactions between sediments and fresh waters. Junk.
- Lijklema, L. 1980. Interaction of ortho-phosphate with iron (III) and aluminum hydroxides. Environ. Sci. Technol. 14:537-541.
- Likens, G.E. (ed.). 1972. Nutrients and eutrophication: The limiting nutrient controversy. Special Symposium, Amer. Soc. Limnol. Oceanogr. 1:328.

- Lonsdale, P., and J.B. Southard. 1974. Experimental erosion of North Pacific red clay. *Mar. Geol.* 17:51-60.
- Madsen, O.S., and W.D. Grant. 1975. The threshold of sediment movement under oscillatory waves: A discussion. *J. Sed. Petrol.* 45:360-361.
- Manheim, F.T. 1970. The diffusion of ions in unconsolidated sediments. *Earth Plan. Sci. Lett.* 9:307-309.
- Martens, C.S., and J.V. Klump. 1980. Biogeochemical cycling in an organic-rich coastal marine basin, I. Methane sediment-water exchange processes. *Geochim. Cosmochim. Acta* 44:471-490.
- Mayer, L.M., and S.P. Gloss. 1980. Buffering of silica and phosphate in a turbid river. *Limnol. Oceanogr.* 25:12-22.
- McAllister, D.L., and T.J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. *J. Environ. Qual.* 7:87-92.
- McCaffrey, P.M., W.W. Hinkley, R. MacGill, and G.D. Cherr. 1976. Report of investigations in the Kissimmee River-Lake Okeechobee watershed. Florida Dept. of Environ. Reg. Tech. Series 2(2).
- McCaffrey, R.J., A.C. Myers, E. Davey, G. Morrison, M. Bender, N. Leudtke, D. Cullen, P. Froelich, and G. Klinkhammer. 1980. The relation between pore water chemistry and benthic fluxes of nutrients and manganese in Narransett Bay, Rhode Island. *Limnol. Oceanogr.* 25:31-44.
- Meyer, J.L. 1979. The role of sediments and bryophytes in phosphorus dynamics in a headwater stream ecosystem. *Limnol. Oceanogr.* 24:365-375.
- Migniot, C. 1968. Etude des proprietes physiques des differents sediments tres fins et de leur comportement sous des actions hydrodynamiques. *La Houille Blanche* 7:591-620.
- Morse, J.W., and N. Cook. 1978. The distribution and form of phosphorus in North Atlantic Ocean deep-sea and continental slope sediments. *Limnol. Oceanogr.* 23:825-830.
- Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes, 1. *J. Ecol.* 29:280-329.
- Mortimer, C.H. 1942. The exchange of dissolved substances between mud and water in lakes, 2. *J. Ecol.* 30:147-201.
- Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31-36.

- Neame, P.A. 1977. Phosphorus flux across the sediment water interface, p. 307-312. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Nisson, J.D. 1975. Sediment-water nutrient dynamics. M.S. thesis, Univ. Florida.
- Obihara, C.H., and E.W. Russell. 1972. Specific adsorption of silicate and phosphate by soils. J. Soil Sci. 23:105-117.
- Oglesby, R.T., and W.R. Schaffner. 1978. Phosphorus loadings to lakes and some of their responses, part 2. Regression models of summer phytoplankton standing crops, winter total P, and transparency of New York lakes with known phosphorus loadings. Limnol. Oceanogr. 23:120-134.
- Olsen, S.R., and F.S. Watanabe. 1957. A method to determine a phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Am. Proc. 21:144-149.
- Petr, T. 1977. Bioturbation and exchange of chemicals in the mud-water interface, p. 216-226. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Pollman, C.D. 1977. Sediment characterization and nutrient dynamics of selected real estate canals. M.S. thesis, Univ. Florida.
- Pollman, C.D., T.L. Crisman, P.L. Brezonik, and P. Sacco. 1980. Limnological studies on Lake Apopka and the Oklawaha chain of lakes, 3. Water quality in 1979. Rept. No. 07-80-02. Dept. of Env. Eng. Sci., Univ. Florida.
- Redfield, A.C., B.J. Ketchum, and F.A. Richards. 1963. The influence of organisms on the composition of seawater, p. 26-77. In M.R. Hill (ed.), The sea, v. 2. Wiley-Interscience.
- Riedel, P.H., and J.W. Kamphuis. 1973. A shear plate for use in oscillatory flow. J. Hydraul. Res. 11:137-156.
- Rippey, B. 1977. The behaviour of phosphorus and silicon in undisturbed cores of Lough Neagh sediments, p. 348-353. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Robbins, J.A., and D.N. Edgington. 1975. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochim. Cosmochim. Acta 39:285-304.
- Ryding, S.O., and C. Forsberg. 1977. Sediments as a nutrient source in shallow polluted lakes, p. 227-234. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.

- Schaffner, W.R., and R.T. Oglesby. 1978. Phosphorus loadings to lakes and some of their responses, Part I. A new calculation of phosphorus loading and its application to 13 New York lakes. *Limnol. Oceanogr.* 23:112-119.
- Schindler, D.W. 1977. Evolution of phosphorus limitation in lakes. *Science* 195:260-262.
- Schindler, D.W., R. Hesslein, and G. Kipphut. 1977. Interactions between sediments and overlying waters in an experimentally eutrophied precambrian shield lake, p. 235-243. In H.L. Golterman (ed.), *Interactions between fresh water and sediments*. Junk.
- Schneider, R.F., and J.A. Little. 1968. Characterization of bottom sediments and selected nitrogen and phosphorus sources in Lake Apopka, Florida. U.S. Dept. of Interior Report, FWPCA, Southeast Water Lab., Athens, Ga. (Mimeo).
- Sheng, Y.P., and W. Lick. 1979. The transport and resuspension of sediments in a shallow lake. *J. Geophys. Res.* 84:1809-1826.
- Shields, A. 1936. Anwendung der Ähnlichkeit-smechanik und Turbulenzforschung auf die Geschiebepbewegung. *Mitteil. Preuss. Versuchsanst. Wasserbau und Schiffbau*. No. 26.
- Shukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong, and R.F. Harris. 1971. Sorption of inorganic phosphate by lake sediments. *Soil Sci. Soc. Amer. Proc.* 35:244-249.
- Sly, P.G. 1978. Sedimentary processes in lakes, p. 65-89. In A. Lerman (ed.), *Lakes: Chemistry, geology, and physics*. Springer-Verlag.
- Sonzogni, W.C., D.P. Larsen, K.W. Maleug, and M.D. Schuldt. 1977. Use of large submerged chambers to measure sediment-water interactions. *Water Res.* 11:461-464.
- Southard, J.B., R.A. Young, and C.D. Hollister. 1971. Experimental erosion of calcareous ooze. *J. Geophys. Res.* 76:5903-5909.
- Sposito, G. 1979. Derivation of the Langmuir equation for ion exchange reactions in soils. *Soil Sci. Soc. Am. J.* 43:197-198.
- Sternberg, R.W. 1972. Predicting initial motion and bedload transport of sediment particles in the shallow marine environment, p. 61-82. In D.P. Swift (ed.), *Shelf sediment transport: Process and pattern*. Dowden.
- Sternberg, R.W., and L.H. Larsen. 1975. Threshold of sediment movement by open ocean waves: Observations. *Deep-Sea Research* 22:299-309.

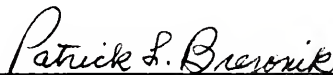
- Stevens, R.J., and C.E. Gibson. 1977. Sediment release of phosphorus in Lough Neagh, Northern Ireland, p. 343-347. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Strayer, R.F., and J.M. Tiedje. 1978. In situ methane production in a small hypereutrophic, hard-water lake: Loss of methane from sediments by vertical diffusion and ebullition. Limnol. Oceanogr. 23(6):1201-1206.
- Stumm, W., and J.O. Leckie. 1971. Phosphate exchange with sediments: Its role in the productivity of surface waters, p. III-26/1-16. In S.H. Jenkins (ed.), Advances in water pollution research. Proc. 5th Int. Conf., San Francisco and Hawaii, v. 2. Pergamon.
- Stumm, W., and J.J. Morgan. 1981. Aquatic chemistry. Wiley-Interscience.
- Terwindt, J.H.J. 1977. Deposition, transportation, and erosion of mud, p. 19-24. In H.L. Golterman (ed.), Interactions between sediments and fresh water. Junk.
- Tessenow, U. 1972. Lösungs-, Diffusions-, und Sorptionprozesse in der Oberschicht von Scesedimenten, I. Ein Langzeitexperiment unter aeroben und anaeroben Bedingungen im Fließgleichgewicht. Arch. Hydrobiol. Suppl. 38:353-398.
- Thibodeaux, L.J. 1979. Chemodynamics: Environmental movement of chemicals in air, water, and soil. Wiley-Interscience.
- Tuschall, J.R., T.L. Crisman, P.L. Brezonik, and J.N. Allison. 1979. Limnological studies on Lake Apopka and the Ocklawaha chain of lakes. 2: Water quality in 1978. Rept. No. ENV-07-79-02. Dept. of Env. Eng. Sci., Univ. Florida.
- Ulen, B. 1978. Seston and sediment in Lake Norvikken, III. Nutrient release from sediment. Schweiz. Z. Hydrol. 40:287-305.
- U.S. Army Coastal Engineering Research Center. 1977. Shore protection manual. v. I. U.S. Army Coastal Engineering Research Center.
- U.S. Environmental Protection Agency. 1976. Methods for chemical analysis of water and wastes. National Environmental Research Center. EPA-625/6-74-003a. U.S. Environmental Protection Agency.
- U.S. Environmental Protection Agency. 1979. Lake restoration. Office of Water and Planning Standards. EPA-440/5-79-001. U.S. Environmental Protection Agency.
- Vallentyne, J.R. 1970. Phosphorus and the control of eutrophication. Can. Res. Development (May-June, 1970):36-43.

- Vanderborght, J.-P., R. Wollast, and G. Billen. 1977. Kinetic models of diagenesis in disturbed sediments, Part 1. Mass transfer properties and silica diagenesis. *Limnol. Oceanogr.* 22(5):787-793.
- Vollenweider, R.A. 1968. Scientific fundamentals of the eutrophication of lakes and flowing waters with particular reference to nitrogen and phosphorus. Tech. Rept. DAS/CSI/68-27. 159 p. (revised 1971). Organisation for Economic Co-Operation and Development.
- Vollenweider, R.A. 1975. Input-output models with special reference to the phosphorus loading concept in limnology. *Schweiz. Z. Hydrol.* 37:53-84.
- Vollenweider, R.A. 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. *Mem. Ist. Ital. Idrobiol.* 33:53-83.
- Wetzel, R.G. 1975. *Limnology*. W.B. Saunders.
- Wildung, R.E., and R.L. Schmidt. 1973. Phosphorus release from lake sediments. EPA-R3-73-024. U.S. Environmental Protection Agency.
- Wildung, R.E., R.L. Schmidt, and A.R. Gahler. 1974. The phosphorus status of eutrophic lake sediments as related to changes in limnological conditions - total, inorganic, and organic phosphorus. *J. Environ. Qual.* 3:133-138.
- Williams, J.D.H., J.M. Jaquet, and R.L. Thomas. 1976. Forms of phosphorus in the surficial sediments of Lake Erie. *J. Fish. Res. Bd. Can.* 33:413-429.
- Williams, J.D.H., H. Shear, and R.L. Thomas. 1980. Availability to Scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. *Limnol. Oceanogr.* 25:1-11.
- Williams, J.D.H., J.K. Syers, and R.F. Harris. 1970. Adsorption and desorption of inorganic phosphorus by lake sediments in a 0.1 M NaCl system. *Environ. Sci. Technol.* 4:517-519.
- Williams, J.D.H., J.K. Syers, S.S. Shukla, R.F. Harris, and D.E. Armstrong. 1971. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. *Environ. Sci. Technol.* 5:1113-1120.
- Yariv, S., and H. Cross. 1979. *Geochemistry of colloid systems*. Springer-Verlag.

BIOGRAPHICAL SKETCH

Curtis D. Pollman was born 2 August 1951 in the small coastal town of Lewes, Delaware. Raised in Seaford, Delaware, he graduated from Seaford Senior High School in June 1969. The following fall he entered the University of Delaware, majoring in biology. During this period Mr. Pollman embarked on a career as a tennis professional, an occupation he pursued in earnest following his graduation with honors in June 1973 with a Bachelor of Arts degree. After a period as a corporate co-owner and head professional of a tennis professional shop in Wilmington, Delaware, he returned to academics and entered the Graduate School of the University of Florida in September 1974, as a student in the Department of Environmental Engineering Sciences. After receipt of a master's degree in early 1977, he continued his graduate career at the University of Florida as a doctoral candidate in the Department of Environmental Engineering Services. He was married to the former Kathleen Doughty in September 1981 and is the doting father of two cats and two golden retriever dogs.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Patrick L. Brezonik, Chairman
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



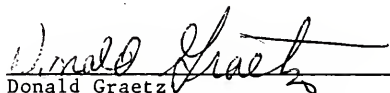
Wayne C. Huber
Professor of Environmental
Engineering Sciences

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

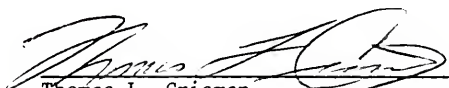


Edward S. Deevey
Graduate Research Professor of
Zoology

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

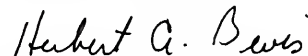

Donald Graetz
Associate Professor of Soil Science

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.


Thomas L. Crisman
Associate Professor of Environmental
Engineering Sciences

This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 1983


Dean, College of Engineering

Dean for Graduate Studies and
Research

UNIVERSITY OF FLORIDA



3 1262 08666 914 9